Inorg. Chem. **2005**, *44*, 843–845

Inorganic Chemistry
Communication

Violation of the Isolated Square Rule for Group 13–15 Oligomers: Theoretical Prediction of a New Class of Inorganic Polymers

Alexey Y. Timoshkin* **and Henry F. Schaefer III**[†]

Inorganic Chemistry Group, Department of Chemistry, St. Petersburg State University, University Pr. 26, Old Peterhof, 198504 Russia, and Center for Computational Chemistry, University of Georgia, Athens, Georgia 30602

Received November 2, 2004

It is widely thought that the oligomer compounds $[RMYR]_n$ (M-group 13, Y-group 15 element) should obey the isolated square rule found for the boron–nitrogen cages. In contrast to these expectations, the needle-shaped oligomers, which violate this rule, are more stable compared to the cage (fullerene-like) oligomers for all MY pairs (M = B, Al, Ga, In; Y = N, P, As). The stability of the needle-shaped clusters improves with increasing oligomerization degree. Thus, the isolated square rule, which is analogous to the isolated pentagon rule widely applied for fullerenes, should not serve as the basis for searches for the most stable structures of the inorganic oligomers. Generation of the needle-shaped oligomers from the group 13 and 15 hydrides is thermodynamically favorable. A synthesis of novel inorganic polymers, formed by fusion of trimeric M_3Y_3 rings, is expected to be viable.

Group 13−15 binary pnictidometallanes $[RMYR']_n$ are promising precursors to 13−15 binary materials, which play an important role in modern microelectronics. While compounds with small oligomerization degrees ($n = 1-8$) are well-known and structurally characterized,[1] the chemistry and structures of the higher oligomers remain almost unexplored. It is widely assumed that $[RMYR]_n$ (M-group 13, Y-group 15 element) oligomer compounds should obey the "isolated square rule"[2] found for the valence-isoelectronic boron−nitrogen cages. This rule is analogous to the "isolated pentagon rule"[3] widely applied for fullerenes, and the rule states that structures with isolated square faces are more stable than those with shared square faces. The isoelectronic methylaluminumoxane (MAO) $[MeAlO]_n$ oligomers were found to obey such a rule,[4] and analogous structures have been considered in previous theoretical studies of $[HMYH]_n$ oligomers.[5,6]

However, the widely used analogy between boron and its heavier analogues may be misleading. For example, dimerization of borazine to form D_{3d} symmetric $[HBNH]_6$ is strongly (by 290 kJ mol^{-1}) endothermic, while dimerization of alumazene and gallazene to form D_{3d} symmetric $[HAlNH]_6$ and $[HGaNH]_6$ is very exothermic (by 460 and 320 kJ mol^{-1}, respectively).[7] Thus, structures observed for the boron−nitrogen chemistry may not be the best choices for the heavier analogues of boron.

The isolated square rule is partially justified by the following argument. In order to obtain a closed cage, an $[HMYH]_n$ structure should possess exactly six square (S) and $(n - 4)$ hexagonal (H) faces, where n is the oligomerization degree. As n increases, the probability that an atom is bound to three square faces becomes very small. So does the probability that an atom is bound to two square faces and one hexagonal face.[4] This trend is of course true if one expands the structure in all dimensions, forming cages. However, one can imagine a series of a needle-shaped structures, obtained by the expansion in one dimension (analogous to nanotubes). The simplest possibility would be adding trimeric M_3Y_3 rings together and capping them on both sides. The well-known $[RMYR']_4$ cubanes[1] are examples of the first member of this series, followed by the structurally characterized heptamers[8] and the proposed,[8a,9]

---

* To whom correspondence should be addressed. E-mail: alextim@AT11692.spb.edu.

[†] E-mail: hfsiii@arches.uga.edu.

(1) (a) Cesari, M.; Cucinella, S. In *The chemistry of inorganic homo- and heterocycles*; Academic Press: London, 1987; Vol. 1, pp 167−190. (b) *Supramolecular Organometallic Chemistry*; Haiduc, I., Edelmann, F. T., Eds.; Wiley-VCH: New York, 1999.

(2) (a) Sun, M.-L.; Slanina, Z.; Lee, S.-L. *Chem. Phys. Lett.* **1995**, *233*, 279. (b) Fowler, P. W.; Heine, T.; Mitchell, D.; Schmidt, R.; Seifert, G. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 2197.

(3) (a) Dinadayalane, T. C.; Sastry, G. N. *Tetrahedron* **2003**, *59*, 8347. (b) Schmalz, T. G.; Seitz, W. A.; Klein, D. J.; Hite, G. E. *J. Am. Chem. Soc.* **1988**, *110*, 1113 (c) Aihara, J.-I.; Oe, S.; Yoshida, M.; Osawa, E. *J. Comput. Chem.* **1996**, *17*, 1387.

(4) Zurek, E.; Woo, T. K.; Firman, T. K.; Ziegler, T. *Inorg. Chem.* **2001**, *40*, 361.

(5) (a) Wu, H.; Zhang, C.; Xu, X.; Zhang, F.; Zhang, Q. *Chin. Sci. Bull.* **2001**, *46*, 1507. (b) Xu, X.-H.; Wu, H.-S.; Zhang, F.-Q.; Zhang, C.-J.; Jin, Z.-H. *J. Mol. Struct.* **2001**, *542*, 239.

(6) Timoshkin, A. Y. *Inorg. Chem. Commun.* **2003**, *6*, 274.

(7) Timoshkin, A. Y.; Frenking, G. *Inorg. Chem.* **2003**, *42*, 60.

(8) (a) Luo, B.; Gladfelter, W. L. *Inorg. Chem.* **2002**, *41*, 590. (b) Cucinella, S.; Salvatori, T.; Busetto, C.; Perego, G.; Mazzei, A. *J. Organomet. Chem.* **1974**, *78*, 185. (c) Driess, M.; Kuntz, S.; Monsé, C.; Merz, K. *Chem. Eur. J.* **2000**, *6*, 4343.

(9) Hitchcock, P. B.; Smith, J. D.; Thomas, K. M. *J. Chem. Soc., Dalton Trans.* **1976**, 1433.

10.1021/ic048468g CCC: $30.25

but yet unknown, needle-shape oligomers with $n = 10$, 13, 16, and so forth. In a recent case study of $[HGaNH]_n$ ($n = 7-16$) oligomers,[10] we showed that the needle-shaped oligomers, which violate the isolated square rule, are more stable than the cage (fullerene-like) oligomers. It was also found that the stability of the needle-shaped clusters is enhanced by increasing degrees of oligomerization.

This surprising discovery prompted us to investigate if the situation holds only for GaN imidogallanes or may be generalized for the other group 13−15 oligomers. To our knowledge, such needle-shaped clusters have been not studied theoretically. We report here relative energies of needle-shaped and cage oligomers $[HMYH]_n$ (M = B, Al, Ga, In; Y = N, P, As; $n = 10$, 13, 16). We also considered the feasibility of the formation of such structures from group 13 and 15 hydrides:

$$H_3M + YH_3 \rightarrow {}^1/_n[HMYH]_n + 2H_2 \qquad (1)$$

Since our primary goal is the description of the large cluster compounds, consisting of 40−64 atoms, the present theoretical approach is based on density functional theory in the form of the hybrid 3-parameter B3LYP functional[11] conjoined with an effective core potential (ECP) LANL2DZ basis set,[12] augemented by d and p polarization functions.[13] The Gaussian[14] suite of programs was used throughout. This level of theory was found to provide an adequate description of the energetics of donor−acceptor complexes of group 13 metal halides with ammonia (mean difference with respect to experiment in dissociation energies 2 kcal mol^{-1}).[15] Preliminary results of this paper have been presented at the 36th ICCC meeting in Merida (July 2004).[16]

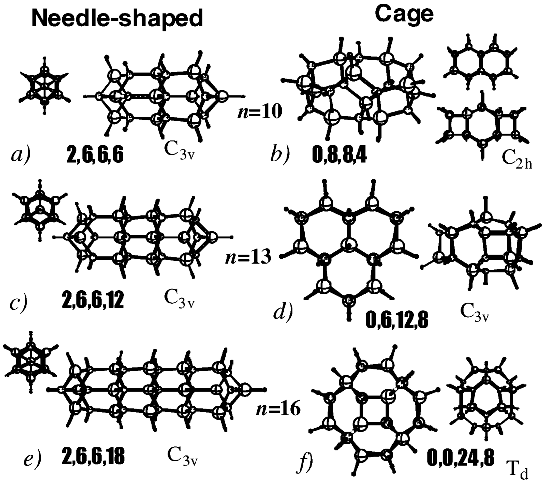

Figure 1. Structures of the needle-shaped (a, c, e) and cage (b, d, f) $[HMYH]_n$ isomers. The four integers below the structures are the numbers of atoms in the 3S, 2S + H, 2H + S, and 3H positions, respectively.

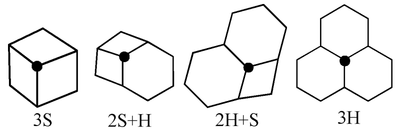

Figure 2. Schematic view of an atom in the 3S, 2S + H, 2H + S, and 3H positions, respectively.

With an increase of the oligomerization degree, the number of possible structural isomers increases dramatically. Since the major goal of the present report is not a characterization of all possible isomers, but an examination of the rivalry between cage and needle-shaped structures, only two isomers for the each oligomerization degree have been considered (Figure 1).

Following the notation used in the work of Ziegler,[4] we will classify isomers by the number of atoms in particular positions: 3S, 2S + H, 2H + S, 3H where 3S refers to the number of atoms sharing three square faces; 2S + H describes those sharing two square faces and one hexagonal face; etc. (see examples in Figure 2).

On the basis of the isolated square rule, structures b, d, and f (Figure 1) are expected to be preferred compared to their counterparts, since the former lacks atoms in the 3S positions. However, in contrast to these expectations, relative energies of the isomers (Table 1) show the opposite trend. Only for $n = 10$ are the needle-shaped and cage isomers close in energy. Moreover, as the oligomerization degree increases, the relative energies of the oligomers substantially increase in favor of the needle-shaped entities for all 13−15 pairs!!! Thus, the isolated square rule is generally not applicable to group 13−15 oligomers. This result also suggests the importance of the needle-shaped clusters in the chemistry of group 13−15 compounds.

What makes the needle-shaped structures so stable? One explanation is the possibility of structural relaxation. While in the cage structures all atoms are strained (in order to form a closed cage), in the needle-shaped structures only the atoms in the capping region (3S and 2S + H positions) are highly strained, and atoms in the middle of the needle (3H positions) are much more relaxed. As n increases, the number of

---

(10) Timoshkin, A. Y.; Schaefer, H. F. *J. Am. Chem. Soc.* **2004**, *126*, 12141−12154.

(11) (a) Becke, A. D. *J. Chem. Phys.* **1993**, 98, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(12) (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270. (b) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284. (c) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

(13) The following d exponents have been used: B 0.6; Al 0.4; Ga 0.16; In 0.16; N 0.8; P 0.5; As 0.25. The p exponent 1.0 was used for H.

(14) (a) 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.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, revision C.3; Gaussian, Inc.: Pittsburgh, PA, 1995. (b) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.3; Gaussian, Inc.: Pittsburgh, PA, 1998.

(15) Timoshkin, A. Y.; Suvorov, A. V.; Bettinger, H. F.; Schaefer, H. F. *J. Am. Chem. Soc.* **1999**, *121*, 5687.

(16) Timoshkin, A. Y. Abstracts of the 36th International Conferece on Coordination Chemistry, July 2004, Merida, Mexico, p 230.

Table 1. Relative Energies E^{rel}'s (kJ mol^{-1}) of the Cage $[\mathrm{HMYH}]_n$ Isomers with Respect to the Needle-Shaped Isomers and Energetics for the Generation of the Needle-Shaped Isomers According to Reaction 1[a]

	$n = 10$		$n = 13$		$n = 16$	
compd	E^{rel}	$\Delta E_{(1)}$	E^{rel}	$\Delta E_{(1)}$	E^{rel}	$\Delta E_{(1)}$
$[\mathrm{HBNH}]_n$	−13.0	−176.5	86.6	−182.7	200.0	−186.7
$[\mathrm{HBPH}]_n$	3.7	−77.8	34.0	−87.1	55.1	−93.1
$[\mathrm{HBAsH}]_n$	−0.2	−53.6	26.9	−62.6	30.1	−68.2
$[\mathrm{HAlNH}]_n$	−0.9	−241.4	73.8	−246.3	84.7	−249.3
$[\mathrm{HAlPH}]_n$	6.8	−129.1	38.0	−134.3	51.8	−137.6
$[\mathrm{HAlAsH}]_n$	4.5	−134.2	30.1	−139.4	37.8	−142.6
$[\mathrm{HGaNH}]_n$	−0.2	−152.7	75.6	−157.3	97.9	−160.2
$[\mathrm{HGaPH}]_n$	8.7	−102.8	40.4	−108.0	58.9	−111.3
$[\mathrm{HGaAsH}]_n$	3.0	−115.2	28.4	−120.4	35.1	−123.6
$[\mathrm{HInNH}]_n$	1.7	−128.9	72.4	−132.9	88.3	−135.4
$[\mathrm{HInPH}]_n$	4.6	−120.5	32.1	−124.9	34.2	−127.6
$[\mathrm{HInAsH}]_n$	0.3	−141.4	21.7	−144.1	15.6	−148.5

[a] B3LYP/LANL2DZ(d,p) level of theory.

strained atoms remains constant, and the number of "relaxed" atoms (in 3S positions) increases. Therefore, the needle-shaped structures became more stable with respect to the cage ones.

We also address the question of feasibility of formation of needle-shaped structures. To this end, the energies of formation from group 13 and 15 hydrides have been obtained (Table 1). Process 1 is exothermic for all clusters. Despite the fact that entropy disfavors formation of large clusters (for GaN the reaction entropy for the process 1 varies from −75 ($n = 10$) to −84 ($n = 16$) J mol^{-1} K^{-1}),[10] the overall standard Gibbs energies of the cluster formation are negative (favorable) for all MY pairs. Thus, the formation of needle-shaped structures is clearly practical thermodynamically.

We propose the following mechanistic pathway for the growth of needle structures, starting from the well-known trimeric $[\mathrm{R_2MYR'_2}]_3$ cyclic compounds (Figure 3).

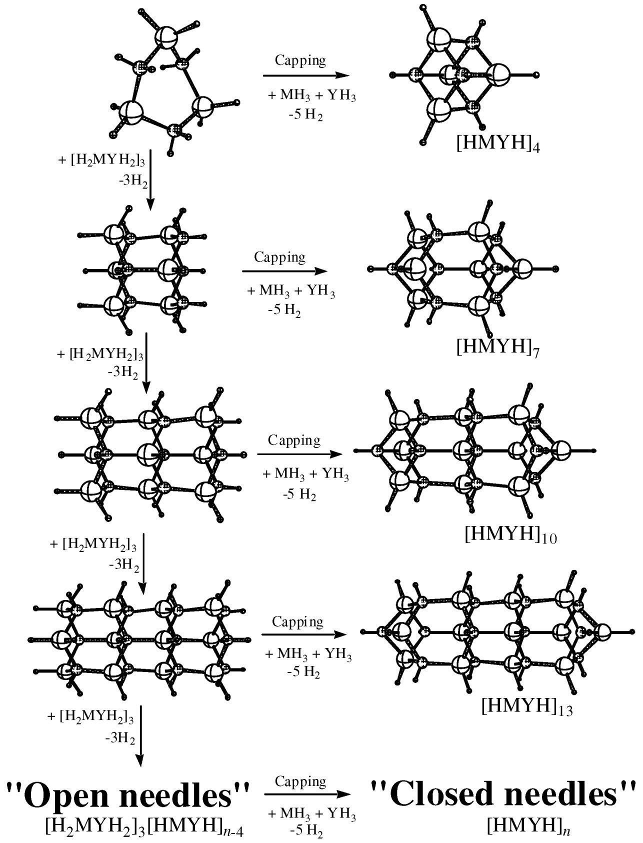

Figure 3. Proposed mechanistic pathway for the formation of needle-shaped oligomer and polymer compounds.

Polymerization of the $[\mathrm{H_2MYH_2}]_3$ units leads to "open needle" oligomers, which on each stage may be capped to form "closed needles". Such polymeric compounds represent a viable alternative to 3-dimensional networks or coordination structures. Recent experiments on the laser-assisted reactivity of $\mathrm{Ga(CH_3)_3}$ and $\mathrm{Al(CH_3)_3}$ with ammonia indeed show that formation of gas-phase oligomers takes place at low temperatures.[17] Thus, the proposed pathway seems viable and may lead to the generation of new inorganic polymers or "nanowires", which may in turn find application in future technologies.

We have shown that the needle-shaped pnictidometallanes with high oligomerization degrees possess greater stability than cage structures. Thus, the "isolated square rule", which is analogous to the "isolated pentagon rule" widely applied for fullerenes, should not serve as the primary basis for searches for the most stable structures.

The generation of gas phase $[\mathrm{HMYH}]_n$ oligomers is very favorable thermodynamically. Spontaneous growth of needle-shaped oligomers is expected under low-temperature conditions for all 13−15 pairs. It is argued that their subsequent nucleation will lead to the formation of corresponding 13−15 nanoparticles. Synthesis of the needle-shaped inorganic nanowires thus appears to be viable.

Acknowledgment. A.Y.T. is grateful to the Alexander-von-Humboldt Foundation for a research fellowship and for a return fellowship. The hospitality of the Philipps-Universität Marburg (Professor Gernot Frenking) is especially appreciated. Financial support of the Educational Ministry of Russian Federation and the St. Petersburg Administration (Grant PD03-1.3-117) is gratefully acknowledged. Work at the University of Georgia was supported by NSF Grant CHE-0136186.

Supporting Information Available: Table containing the total energies of the investigated compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

IC048468G

---

(17) Demchuk, A.; Simpson, S.; Koplitz, B. *J. Phys. Chem. A* **2003**, *107*, 1727.