
The Structure of Small Gallium Nitride Clusters

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ABSTRACT: *The geometry, vibrational frequencies and stability of the structural isomers of small gallium nitride clusters ($n = 2-4$) have been investigated using density functional theory. The lowest energy structures are cyclic. The ground electronic state of the cyclic forms for $n > 2$ is the singlet state. All of the cyclic structures have D_{nh} symmetry. The caged structures for Ga_nN_n lie higher in energy than the planar cumulenic monocyclic ring. The Ga-N bond dominates the structures for many isomers, so that one dissociation channel is loss of a GaN monomer. However, unlike the corresponding boron and aluminum clusters, dissociation into larger fragments is energetically favored. The structural properties of the gallium nitride clusters are similar to those of the analogous AlN (and BN) clusters. © 2000 John Wiley & Sons, Inc. Heteroatom Chem 11:281-286, 2000*

INTRODUCTION

Gallium nitride is a valued material in the microelectronics industry. GaN has been employed as a buffer layer in device fabrication [1], as a component in quantum well formation [2], and as a wide-band semiconductor [3]. The nitride may be produced by chemical vapor deposition from organometallic precursors [4]. More recently, GaN has been formed by nitrogen ion beam bombardment of a gallium target [5], and the potential for cluster formation in this and related experiments is present. To date, sym-

metric clusters of GaN have not been explored by ab initio or density functional theory (DFT) methods.

A second rationale for the study of Ga_nN_n is as a comparison with the recently published results from a number of laboratories on the structures of the analogous B_nN_n clusters [6-10] and our recent study of Al_nN_n [11]. The interest in the boron clusters stems from the possibility of observing fullerene-like molecules assembled from the isoelectronic BN monomer. The potential existence of stable caged gallium nitride structures is of interest for their chemical and physical properties as well as for fundamental studies of chemical bonding. Finally, the study of clusters provides a means to develop an understanding of the nucleation transition of gas phase species into the condensed phase.

In this report, we describe DFT results for small clusters of GaN. The geometric structures, electron configurations, harmonic frequencies, and chemical bonding and cluster stabilities are presented. Comparison is made with the analogous results for AlN and BN clusters.

COMPUTATIONAL DETAILS

All of the reported calculations employed the Amsterdam Density Functional suite of programs (ADF 2.3.0) developed by Baerends et al. and Baerends and te Velde [12,13]. All atomic orbitals were represented by uncontracted triple- ζ STO basis sets with single polarization functions (basis set IV within ADF). The nitrogen 1s and the gallium orbitals through 3p were assigned to the core and treated by the frozen core approximation [12]. In this approximation, the core

orbitals are linear combinations of STOs and are selected so as to be orthogonal to the valence orbitals. The variational treatment of the wavefunction is applied only to the valence electrons after the valence basis set has been enlarged by the number of STOs in the core orbitals. The field due to the core is calculated in the first cycle, remains constant, and is used in all subsequent cycles. A set of auxiliary *s*, *p*, *d*, *f*, and *g* STO functions, centered on all nuclei, was used to fit the electron density and Coulomb and exchange potentials in the SCF cycles [14]. The Vosko-Wilk-Nusair [15] parameterization of the local density approximation was used along with gradient corrections to exchange as proposed by Becke [16] and to correlation as developed by Lee-Yang-Parr [17]. Geometry optimizations were carried out in the absence of symmetry constraints using the unrestricted formalism. Harmonic vibrational frequencies were obtained for all ground state structures as well as a number of other structures of interest. In ADF, these frequencies are calculated via numerical differentiation of energy gradients using slightly displaced geometries [18].

RESULTS AND DISCUSSION

Geometry Optimization

ADF does not calculate absolute energies; rather, the atomization energies are minimized by the structure optimizations. The energies are reported with respect to reference fragments, which in our case are the atoms. Structural parameters and atomization energies are presented in Table 1 for all isomers and spin states examined. Figures 1 through 3 contain pictorial representations of the geometries for all of the clusters.

GaN. We have included electronic structure calculations on the monomer for comparison with other computational methods. Our data indicate that the lowest energy structure corresponds to a molecule in a $^3\Sigma^-$ state with a bondlength of 2.011 Å and an harmonic frequency of 504 cm^{-1} . There are no experimental values available. The most recent calculation [19] performed at a high level of theory indicates that the $^3\Sigma^-$ state lies 0.5 eV below the $^3\Pi$ level. These authors report a bondlength of 1.914 Å and an harmonic frequency of 548 cm^{-1} . Our results indicate that the singlet state lies 0.2 eV above the ground state and has a compressed bondlength, relative to the ground triplet state, of 1.872 Å.

Ga₂N₂. We have examined four possible structural isomers for the dimer: two different rhombic forms of N-Ga-N-Ga, (I) and (II); linear N-Ga-N-Ga,

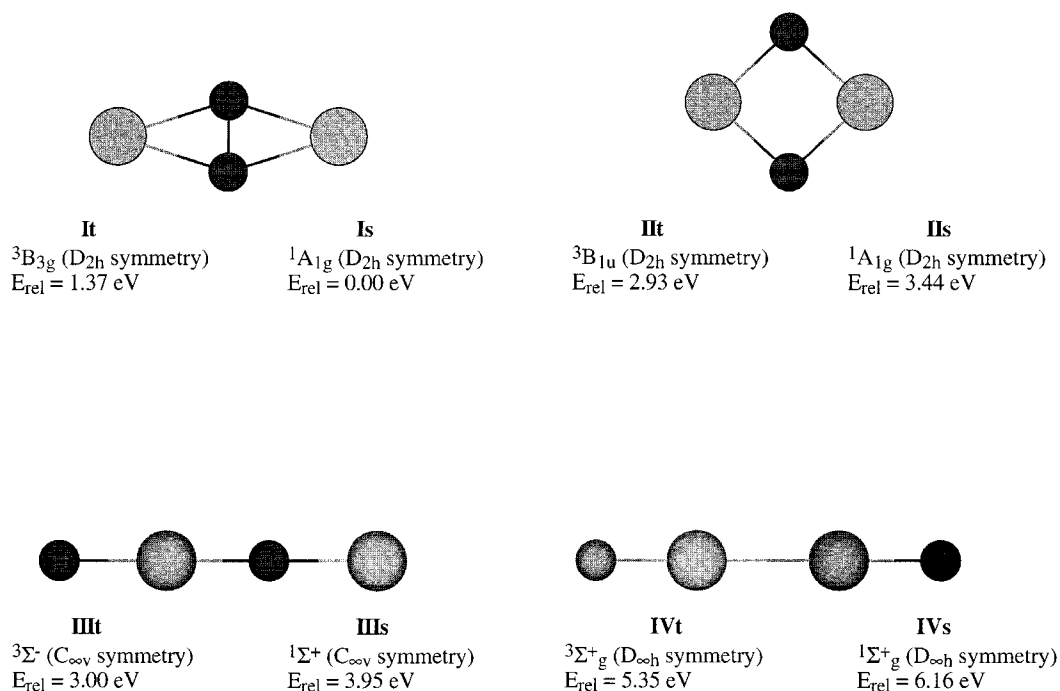
(III); and linear N-Ga-Ga-N, (IV). The lowest energy structure, (Is), corresponds to a totally symmetric singlet state with a rhombic geometry in which the nitrogen atoms lie along the short axis. In this configuration, the N–N bondlength, 1.248 Å, is indicative of a double bond. The overall structure is best classified as gallium end-capped N₂. A similar structure was reported for the valence isoelectronic Al₂N₂ and Al₂P₂ molecules [11,20]. The importance of N–N bonding is evident when the N–N distance is systematically increased while the Ga–Ga bondlength is decreased. The energy of the molecule increases as these changes are made, but SCF convergence fails if the Ga–Ga distance is shortened beyond a certain limit. Optimization from a starting geometry intermediate between the extremes of N₂ bonding and the limit of the Ga–Ga distance results in an optimized structure, (IIIt), with Ga–N bondlengths similar to the bondlength of the monomer and a Ga–Ga distance, 2.841 Å, somewhat longer than that in bulk gallium [21], but in the range of the values reported [22] for Ga₂. The singlet structure (IIIs) lies approximately 0.3 eV above the triplet state. The end-capped triplet It is 1.41 eV higher in energy than its corresponding singlet state. In a previously reported Al₂P₂ study [20], the structure similar to Is was described as covalently bonded, whereas the singlet analogous to IIIt was nearly ionic. Examination of the Mulliken populations indicates a similar trend in the case of Ga₂N₂. The charges on Is are ± 0.36 , and those for IIIt are ± 0.56 .

Ga₃N₃. For the linear conformation, we optimized only the alternating Ga–N–Ga–N–Ga–N configuration, since our experience with the dimer indicated that the configuration having a Ga–Ga bond was considerably higher in energy. For this structural isomer, (VII), the triplet lies lower in energy than the singlet. The global lowest energy isomer is the D_{3h} hexagonal structure, (Vs). This singlet state lies approximately 0.5 eV below the corresponding triplet state and 0.2 eV below the triplet state of the linear isomer. The general structure consists of a pair of concentric Ga₃ and N₃ triangles. The Ga–N bondlength is somewhat shorter than that observed in the dimer. The Ga–Ga distance in the ground singlet state is 2.618 Å, which is within the range of calculated bondlengths reported for the gallium dimer (2.583–2.762 Å) [22]. An alternative interpretation of this structure is as an equilateral Ga₃ which is end-capped by nitrogen atoms on each side. In order to assess the potential importance of gallium-gallium interaction, the Ga-Ga separation was increased while simultaneously decreasing the N–N distance. The energy increases as these distances are changed

TABLE 1 Structural Parameters and Atomization Energies for the GaN Clusters Using the B3LYP Functional and a Triple ζ Basis Set with Single Polarization Functions

Structure	Spin	$r_{\text{Ga-N}}$ (Å)	$r_{\text{Ga-Ga}}$ (Å) ^a	$\angle \text{N-Ga-N, deg}$ ($\angle \text{Ga-N-Ga, deg}$)	Energy (eV)
Ga₂N₂					
rhombus (I)	0	2.216	1.248 _{N-N}	32.7 (147.3)	-11.60
	1	2.219	1.313 _{N-N}	34.4 (145.6)	-10.23
rhombus (II)	0	1.905	3.015	75.4 (104.6)	-8.16
	1	1.939	2.841	85.9 (94.2)	-8.67
linear (III)	0	1.827	—	180.0	-7.65
	1	1.827	—	180.0	-8.60
linear (IV)	0	1.786	2.450	180.0	-5.44
	1	1.799	2.419	180.0	-6.25
Ga₃N₃					
hexagon (V)	0	1.864	2.618	150.8 (89.2)	-14.78
	1	1.880	2.817	134.0 (106.0)	-14.31
hexagon (VI)	0	2.171	1.509 _{N-N}	40.7 (160.7)	-13.81
linear (VII)	0	1.738	—	180.0	-13.37
	1	1.785	—	180.0	-14.14
Ga₄N₄					
octagon (VIII)	0	1.823	2.775	170.9 (99.2)	-22.17
	1	1.836	2.946	163.3 (106.7)	-21.12
cube (IX)	0	2.032	2.856	90.7 (89.3)	-19.59
	1	2.033	2.859	90.7 (89.3)	-20.14
linear (X)	0	1.761	—	180.0	-18.94
	1	1.765	—	180.0	-19.63

^aN-N implies that the value shown is for an N-N rather than Ga-Ga bond.

**FIGURE 1** Lowest energy structures and relative energies for the Ga₂N₂ isomers. The darker atoms represent nitrogen.

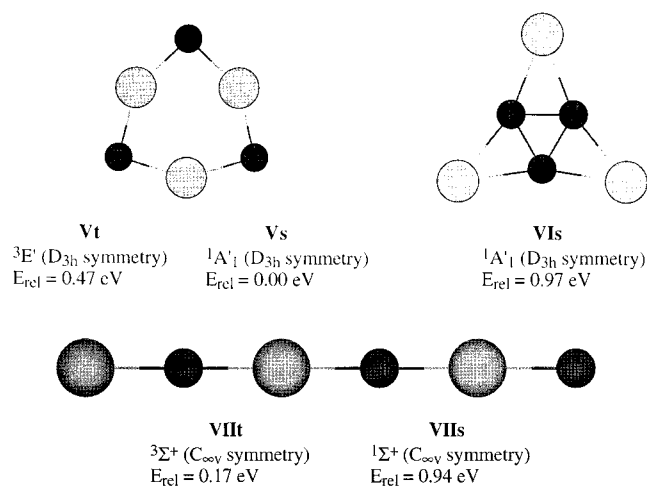


FIGURE 2 Lowest energy structures and relative energies for the Ga_3N_3 isomers. The darker atoms represent nitrogen.

and a singlet state (but no triplet state) stationary point, (VIIs) was located approximately 1 eV above the ground state trimer. The indication is that Ga-Ga interaction is significant and contributes to the stabilization of this geometry. Mulliken population analysis of **V** indicated charges of ± 0.69 , so this structure is highly ionic in character.

Ga_4N_4 . The planar ring, (VIII), and as well as the three dimensional cubic structure, (IX), and the alternating linear isomer, (X), were optimized. The lowest energy structure is the ring in the singlet electronic state. This isomer, as with the trimer, consists of concentric fragments of Ga_4 and N_4 . The linear structure is the highest energy configuration from among those examined. The Ga-Ga distance in the ground singlet state is comparable to that discussed for the trimer and significant metal-metal interaction is likely in this cluster. Mulliken population analysis indicated charges of ± 0.83 , in the range expected for a structure with strong ionic character.

Examination of the MO composition of the isomers provides some indication of the rationale leading to the calculated ground states. For $n = 3$ and 4, it is only for the cyclic structure and then only for the singlet electronic state, that a HOMO consisting of out-of-plane p-orbitals, involving mostly nitrogen orbitals with a small contribution from the gallium atom, is available. The ground state structure, therefore, exhibits what might be described as a pseudo- π orbital system which confers additional stability to the ring conformer. For the case of the dimer, in which the ring is still a necessary condition for stability, the pseudo- π system is composed of nitrogen orbitals exclusively and only the triplet state pro-

vides the orbital configurations to result in the appropriate MO.

Cluster Stability

For the remainder of the discussion, we focus on the minimum energy structural isomers for each cluster size. These include two different structures for the dimer, (Is) and (IIIt), one isomer for the trimer, (Vs), and one for the tetramer, (VIIIIs). Two structures are included for the dimer, since one, (IIIt), is analogous to those for the higher order clusters and the second, (Is), is the true minimum energy isomer. The singlet-triplet energy differences for the most stable geometries, the cyclic isomers, are smaller than those for the analogous aluminum nitride clusters, but significant. Values of 1.37 eV (for the N-N bonded isomer), 0.51 eV, 0.47 eV and 1.05 eV, respectively, were calculated for the dimer, trimer, and tetramer. These differences reflect the relative stability of the clusters to reaction. For the most stable isomers of Ga_2N_2 , Ga_3N_3 , and Ga_4N_4 , the atomization energies are 11.60 eV (for the N-N bonded structure), 8.67 eV, 14.78 eV, and 22.17 eV, respectively. The increasing atomization energies indicate that the formation of the clusters is a favorable process. If we restrict our consideration to only the clusters described in this report, we obtain the possible fragmentation processes shown in Table 2 for spin-allowed reactions. The fragmentation energy for the minimum energy dimer cluster, (Is), corroborates the interpretation of this structure as an end-capped N_2 , since the dissociation energy for production of N_2 and atomic gallium is small. The average Ga-N bond energy in this cluster is only 15% of that in the remaining clusters. For the clusters with analogous geometry, (IIIt), (Vs), and (VIIIIs), the $n = 2$ and 3 clusters would be expected to fragment by loss of a monomeric Ga-N unit. However, for the $n = 4$ clusters, formation of two dimeric units is expected to compete with this process.

Frequencies

The harmonic vibrational frequencies of the lowest energy isomer for each cluster were calculated and are presented in Table 3. The dimer, (IIIt), has three infrared active modes with approximately equal predicted intensity. The trimer (Vs) and tetramer (VIIIIs) each have four IR active vibrational modes. For all three clusters, one mode (b_{1u} for the dimer, a_2'' for the trimer, and a_{2u} for the tetramer) is an out-of-plane motion and this vibration is predicted to exhibit the highest spectral intensity. The out-of-plane modes

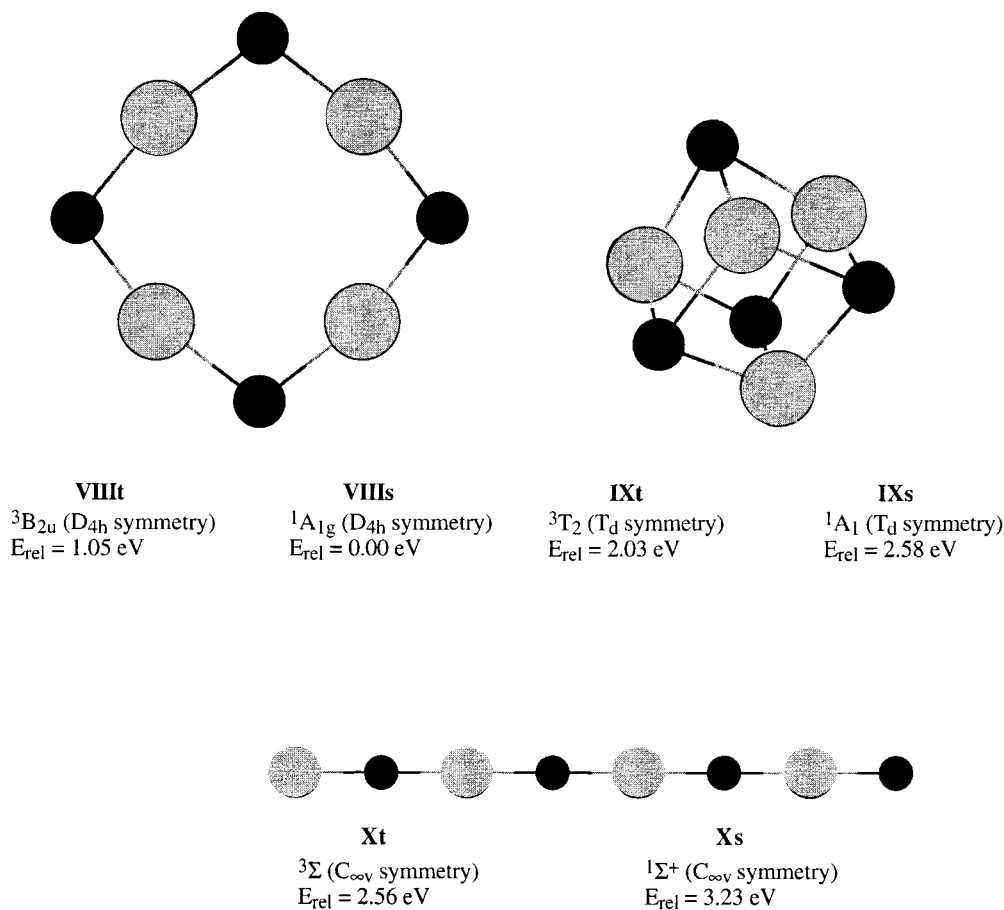


FIGURE 3 Lowest energy structures and relative energies for the Ga_4N_4 isomers. The darker atoms represent nitrogen.

TABLE 2 Dissociation Energetics for the Gallium Nitride Clusters

Reaction	Energy (eV)
$\text{Ga}_2\text{N}_2(\text{Is}) \rightarrow 2\text{Ga-N}({}^3\Pi)$	6.85
$\rightarrow 2\text{Ga-N}({}^1\Sigma^+)$	8.57
$\rightarrow 2\text{Ga}({}^2P) + \text{N}_2({}^1\Sigma_g^+)$	1.23
$\text{Ga}_2\text{N}_2(\text{IIIt}) \rightarrow 2\text{Ga-N}({}^3\Pi)$	3.82
$\rightarrow \text{Ga-N}({}^3\Pi) + \text{Ga-N}({}^1\Sigma^+)$	4.68
$\text{Ga}_3\text{N}_3(\text{Vs}) \rightarrow 3\text{Ga-N}({}^1\Sigma^+)$	10.08
$\rightarrow \text{Ga-N}({}^1\Sigma^+) + \text{Ga}_2\text{N}_2({}^1A_{1g})$	5.05
$\rightarrow \text{Ga-N}({}^3\Pi) + \text{Ga}_2\text{N}_2({}^3B_{1u})$	3.69
$\text{Ga}_4\text{N}_4(\text{VIIIIs}) \rightarrow 4\text{Ga-N}({}^1\Sigma^+)$	15.91
$\rightarrow \text{Ga-N}({}^1\Sigma^+) + \text{Ga}_3\text{N}_3({}^1A_1')$	5.83
$\rightarrow 2\text{Ga}_2\text{N}_2({}^1A_{1g})$	5.85
$\rightarrow 2\text{Ga}_2\text{N}_2({}^3B_{1u})$	4.83

TABLE 3 Harmonic Frequencies (cm^{-1}) of Ground State Clusters^a

Ga-N (${}^3\Sigma^-$)	504 (a)
(Is) Ga_2N_2 (${}^1A_{1g}$)	112 (b_{1u}); 135 (b_{3u}); 160 (a_{1g}); 418 (b_{2u}); 447 (b_{1g}); 1418 (a_{1g})
(IIIt) Ga_2N_2 (${}^3B_{1u}$)	238 (b_{1u}); 244 (a_{1g}); 392 (b_{2u}); 398 (b_{3u}); 495 (b_{1g}); 608 (a_{1g})
(Vs) Ga_3N_3 (${}^1A_1'$)	42 (e_1'); 180 (a_2'); 190 (e_1'); 272 (a_1'); 519 (e_1'); 593 (a_1'); 574 (a_2'); 640 (e_1')
(VIIIIs) Ga_4N_4 (${}^1A_{1g}$)	95 (b_{1g}); 96 (b_{1u}); 112 (b_{2g}); 116 (b_{2u}); 185 (e_g); 203 (e_u); 209 (a_{1g}); 224 (a_{2u}); 581 (e_u); 582 (a_{1g}); 644 (b_{2g}); 712 (b_{1g}); 713 (a_{2g}); 790 (e_u)

^aInfrared active modes are noted in bold.

are very low in frequency. The remaining IR active vibrations, all of which exhibit moderate spectral intensities, are of e_u or e_1' symmetry and represent in plane distortions of the ring. We consider dimer (Is) separately. This dimer has the same harmonic mo-

tions as the other rhombic isomer, but the energies are quite different. Most importantly, the frequency of the a_{1g} stretch, which occurs along the short N–N axis, is indicative of the strong bonding interaction in this direction.

Comparisons with Carbon and Boron Nitride Clusters

The end-capped N_2 structure observed for the dimer has not been observed for boron [11]. However, a similar geometry has been reported as the minimum energy configuration for Al_2N_2 [11], Al_2P_2 [20], and Si_4 clusters [23]. The Si–Si, N–N, and P–P bonds across the short axis of their respective rhombic structures are typical of those expected for a double bond. In the homonuclear Si clusters, the end-capped bond distances are close to those expected from the bulk parameters of Si, and the heteronuclear aluminum (and gallium) clusters have very weak bonds across the long axis.

Two computational studies [24,25] have been reported for small boron nitride clusters. Both of these studies find that cumulenic D_{nh} rings are the preferred structural form for small clusters, including the dimer. This result, which is, in general, similar to that reported here for the gallium nitride clusters, is somewhat surprising in light of the atomic radius difference between Ga and B. For comparison purposes of the radius effect, we can compare BN clusters to carbon clusters, as well as carbon to silicon clusters. Atomic radius certainly plays a role in the variation in the observed molecular geometry when carbon and silicon clusters are compared. The expectation, borne out by experiment, was that BN clusters and C clusters would exhibit similarities based on size [25] and the isoelectronic principle [24,25]. GaN, AlN, and BN clusters should not necessarily be expected to show structural similarities because the difference in atomic radius is comparable to that observed for Si and C, and the latter difference produces changes in cluster geometry. The 50% increase in atomic radius between carbon and silicon contributes to the observation that even small ($n > 3$) Si_n clusters exhibit caged structures rather than cumulenic rings as observed in carbon clusters of similar size [26]. A change in atomic radius for the Group III nitrides of a magnitude similar to that for Group IV clusters appears to have almost no effect on their structural properties. The comparisons between $(GaN)_n$, $(AlN)_n$, and $(BN)_n$ indicate that gallium nitride fullerene structures may be pos-

sible for the same clusters sizes as have been predicted or observed for boron nitride.

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