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Density Functional Theoretical Study of a Series of Binary Azides $M(N_3)_n$ ($n = 3, 4$)

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Geometrical structures of a series of binary azides $M(N_3)_n$ (M = elements in groups 3 and 13 ($n = 3$) and in groups 4 and 14 ($n = 4$)) were investigated at the B3LYP/6-311+G* level of theory. Our calculations found that binary group 3 triazides $M(N_3)_3$ (M = Sc, Y, La) and binary group 4 tetraazides $M(N_3)_4$ (M = Ti, Zr, Hf) turn out to be stable with all frequencies real having a similar linear M−N−NN structural feature, as previously reported for $M(N_3)_4$ (M = Ti, Zr, Hf). However, binary azides of group 13 $M(N_3)_3$ (M = B, Al, Ga, In, Tl) and group 14 elements $M(N_3)_4$ (C, Si, Ge, Sn, Pb) with bent M−N−NN bond angles differ obviously from binary group 3 and 4 azides in geometrical structure. These facts are mainly explained by the difference in electronic density overlap between the central atom and the α-N atoms of the azido groups. Two lone-pair electrons on the sp hybridization α-N atoms in the binary group 3 and 4 azides donate electron density into two empty d orbitals of the central transition metal atom and a pair of valence bonding electrons, resulting in the α-N atoms acting as a tridentate ligand. The sp^2 hybridization α-N atoms of the binary group 13 and 14 azides only give one valence electron to form one valence bonding electron pair acting virtually as monodentate donors.

1. Introduction

Since every azido group adds about 70 kcal/mol to the energy content of the molecule, binary azides with a high number of azido groups might be potential high-energy density materials (HEDMs). However, their synthesis, isolation, and structural characterization present many experimental challenges due to their explosive nature and shock sensitivity.[1−5] Recently, despite many difficulties, some very significant advances were made in the field of highly energetic binary azides.[1,4,5] In 2003, Klapötke and co-workers reported the synthesis, isolation, and properties of binary covalent polyazide $Te(N_3)_4$ and described its explosive nature and potential danger.[1] Another recent theoretical study predicted that binary azides $M(N_3)_4$ (M = Ti−Hf, Th) exhibit a unique tetrahedral linear M−N−NN structural feature,[4] which are obviously different from other binary azides previously reported with bent M−N−NN bond angles. More recently, Haiges et al.[5] further reported the synthesis, isolation, and characterization of the first binary group 4 azides $Ti(N_3)_4$ in their experiments. Although all their attempts to obtain $Ti(N_3)_4$ single crystals by recrystallization or sublimation were unsuccessful, the occurrence of linear Ti−N−NN bond angles was confirmed by independent computations. This unique linear M−N−NN structural feature was explained by a nearly ideal overlap between three valence electron pairs on the α-N atoms of the azide ligands and the d orbitals of the central atom.

A novel high-energy triazidocarbenium cation $C(N_3)_3^+$, when combined with N_3^- again to form $C(N_3)_4$, might also be an ideal HEDM due to the existence of more numbers of highly energetic azido groups.[6] To date, only the ions $C(N_3)_3^+$ and $M(N_3)_6^{2-}$ (M = Si, Ge, Sn, Pb) were structurally characterized[7−12] and $Si(N_3)_4$ was reported to be a violently explosive substance,[13] but no structural information on $M(N_3)_4$ (M = C, Si, Ge, Sn, Pb) has been reported systemically in theory. Moreover, $B(N_3)_3$, $Al(N_3)_3$, and $Ga(N_3)_3$ were reported to be sensitive compounds in previous papers,[14−16] but their structural characters were not theoretically studied in detail, except for $B(N_3)_3$.[17]

Therefore, a series of binary group 3, 4 and group 13, 14 azides are investigated using the density functional theory (DFT) to better explain their different geometrical structural features in the present paper. Up to now, there are no reports about binary group 3 triazides. The calculated results indicate that these molecules turn out to be stable with all frequencies real but present different M−N−NN structural feature between the group 3, 4 and group 13, 14 binary azides. To further explain their remarkable difference in geometrical structure, their natural bond orbital (NBO) analyses are given in the present paper.

2. Calculation Methodology

DFT has proven to be very powerful because the Kohn−Sham orbitals turn to be more helpful for a bonding analysis in terms of orbital interactions than the Hartree−Fock orbitals, since the former include correlation effects. The group 3, 4 and group 13, 14 binary azides were studied using the density functional theory (DFT). Their equilibrium geometrical structures and harmonic vibrational frequencies were computed at the B3LYP/6-311+G* level of theory. B3LYP is a DFT method using Becke's three-parameter nonlocal exchange functional along with additional local correlation corrections attributable to Lee, Yang, and Parr.[18,19] 6-311+G* is a standard split-valence triple-ζ polarization basis set augmented with a diffuse function used for nitrogen atoms and lighter atoms, and the energy-adjusted Stuttgart effective core potentials (ECPs) of the Stuttgart/Dresden group (SDD) basis set is included for the fifth and sixth row heavier atoms (M = Zr, Hf; Sn, Pb; Y, La; In, Tl).[20−22] Last, the natural population and molecular orbital analyses of four typical molecules $M(N_3)_4$ (M = Ti and Ge) and $M(N_3)_3$ (M = Sc and Ga) are presented using the natural

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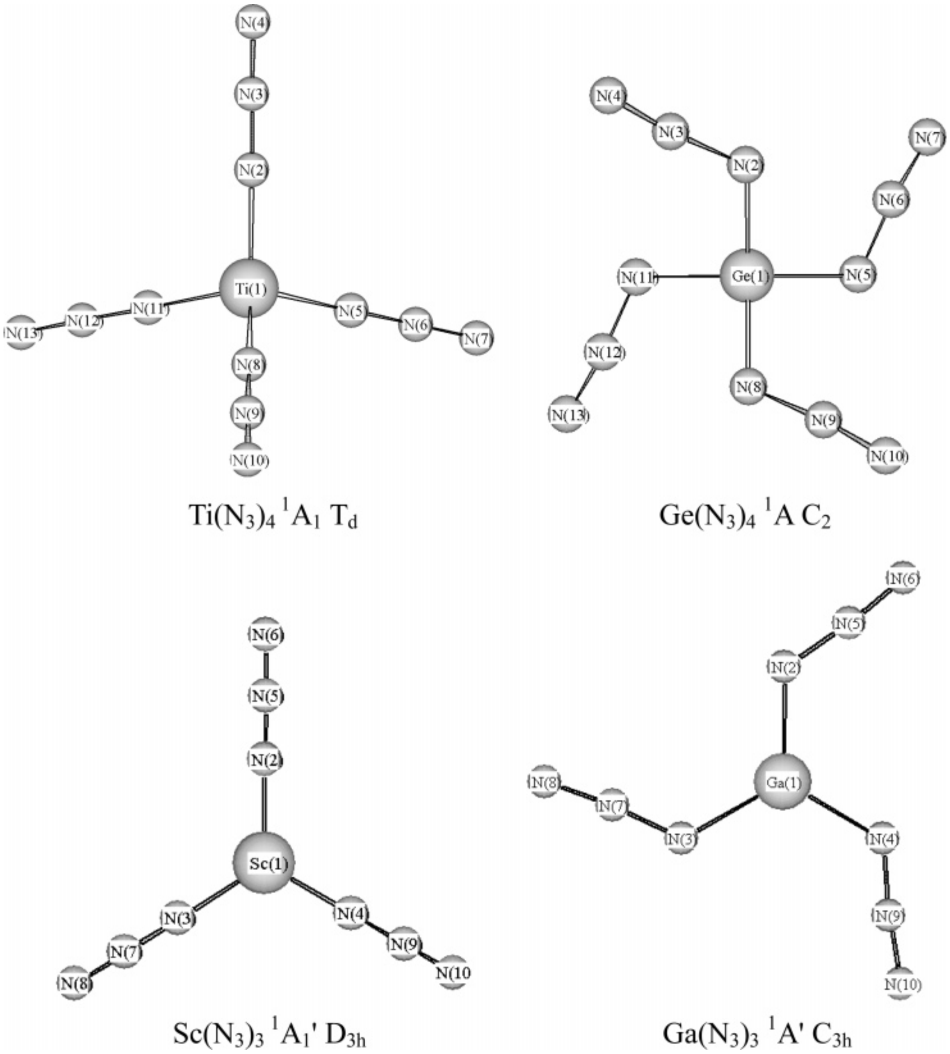

$Ti(N_3)_4\ ^1A_1\ T_d$ $Ge(N_3)_4\ ^1A\ C_2$

$Sc(N_3)_3\ ^1A_1'\ D_{3h}$ $Ga(N_3)_3\ ^1A'\ C_{3h}$

Figure 1. Optimized geometrical structures of four typical binary azides $Ti(N_3)_4$, $Ge(N_3)_4$, $Sc(N_3)_3$, and $Ga(N_3)_3$.

bond orbital procedure (NBO).[23,24] All MOs diagrams were made using the GVIEW 3.07 program. Our calculations were performed using the Gaussian 03 program package.[25]

3. Results and Discussion

3.1. Geometrical Structures of Binary Tetraazides $M(N_3)_4$. Binary group 14 tetraazides $M(N_3)_4$ (M = C, Si, Ge, Sn, Pb) are calculated at the B3LYP/6-311+G* level of theory. For comparison, binary group 4 tetraazides $M(N_3)_4$ (M = Ti, Zr, Hf) are optimized again at the same level of theory, whose geometrical structures were reported at the B3LYP/6-31G* level in a previous paper.[4] In the present paper, the optimized geometries of only $Ti(N_3)_4$ and $Ge(N_3)_4$ are shown in Figure 1, and the other $M(N_3)_4$ (M = Zr, Hf; C, Si, Sn, Pb) molecules with similar structures are not exhibited again. Typical bond parameters of all molecules are summarized in Tables 1 and 2.

Two typical molecules $Ti(N_3)_4$ and $Ge(N_3)_4$ shown in Figure 1 are obviously different in their geometrical structures, particularly in the α-N atom fragment. The M−N−NN fragment of the binary group 4 azides $Ti(N_3)_4$ is linear, as previously reported.[4] The obtained results listed in Table 1 are very close to the previously reported ones for $M(N_3)_4$ (M = Ti, Zr, Hf) at the same B3LYP level, which indicates that the present optimized geometrical structures are reasonable. Among them, the Hf−N_α bond lengths exhibited in Table 1 are very close to those of Zr−N_α because of their similar metal atomic radii of Zr (1.45 Å) and Hf (1.44 Å).[26] All our attempts to obtain bent $M(N_3)_4$ (M = Ti, Zr, Hf) structures finally collapse into their linear geometries. The single-point calculations indicate that all bent structures are higher in energy than their stable linear ones by 22.2, 23.3, and 39.8 kcal/mol, respectively. Their completely planar D_{4h} structures with imaginary frequencies are found to lie 43.1, 40.6, and 41.1 kcal/mol above the stable linear ones, respectively. The triplet state structures of $Ti(N_3)_4$ is calculated to be much higher by 60.3 kcal/mol in energy than its singlet

TABLE 1: Bond Parameters for $M(N_3)_4$ (M = Ti, Zr, Hf) Species at the B3LYP Level of Theory (Bond Length (Å); Bond Angle and Dihedral Angle (deg); Previously Reported Results in Parentheses)

	$Ti(N_3)_4$	$Zr(N_3)_4$	$Hf(N_3)_4$
M1−N2	1.877 (1.879)	2.039 (2.030)	2.033 (2.023)
N2−N5	1.205 (1.203)	1.207 (1.204)	1.207 (1.204)
N5−N6	1.137 (1.135)	1.136 (1.131)	1.135 (1.131)
M1−N2− N3	180.0	180.0	180.0
N2−M1−N5−N8	120.0	120.0	120.0

TABLE 2: Bond Parameters for $M(N_3)_4$ (M = C, Si, Ge, Sn, Pb) Species at the B3LYP Level of Theory

	$C(N_3)_4$	$Si(N_3)_4$	$Ge(N_3)_4$	$Sn(N_3)_4$	$Pb(N_3)_4$
M1−N2	1.467	1.725	1.847	2.047	2.205
N2−N3	1.241	1.226	1.233	1.229	1.230
N3−N4	1.127	1.128	1.130	1.132	1.136
N3−N2−M1−N8	72.3	81.5	82.7	84.4	87.6
N3−N2−M1−N5	168.8	160.4	159.6	158.1	154.7

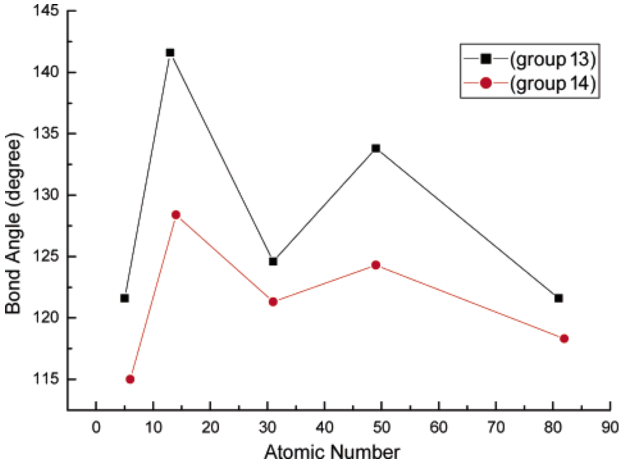

Figure 2. $M-N_\alpha-N_\beta$ bond angle as a function of the atomic number of M in group 13 and 14 binary azides.

ground state, which is very good agreement with a reported value (60 kcal/mol) in the literature.[4] The triplet states of $Zr(N_3)_4$ and $Hf(N_3)_4$ by our calculations are also very higher in energy by 85.9 and 94.8 kcal/mol than their singlet states, respectively. Moreover, the dissociation energy of the linear $Ti(N_3)_4$ molecule for loss of one azide group is 181.2 kcal/mol, which indicates this dissociation reaction is strongly endothermic.

As shown for $Ge(N_3)_4$ in Figure 3, the geometrical structures of the binary group 14 azides $M(N_3)_4$ (M = C, Si, Ge, Sn, Pb) are bent with M−N−NN bond angles, which are similar to some well-known anionic tetraazides, such as $Zn(N_3)_4^{2-}$ confirmed by theoretical calculations, but differ remarkably from the linear binary group 4 azides $Ti(N_3)_4$.[4] The binary group 14 tetraazides are found to be all local minima in C_2 symmetry, and their bond parameters are only slightly different from each other at the B3LYP level of theory, except for the $M-N_\alpha$ bond parameter. Along the C−Pb series, the $M-N_\alpha$ bond distances shown in Table 2 increase with an increase of the atomic radii of M. The $C-N_\alpha$ bond distances of 1.467 Å in $C(N_3)_4$ molecule are longer by 0.11 Å than those observed in $C(N_3)_3^+$,[6] suggesting a different bonding in the two molecules. The $Si-N_\alpha$ bond distances of 1.725 Å for $Si(N_3)_4$ are shorter by 0.15 Å than those reported for S_2 symmetry $Si(N_3)_6^{2-}$,[7] but are very close to those found for tetrahedral azidosilanes ($Si-N_\alpha = 1.760$ Å).[8,9] It suggests that the chemical bonding $Si-N_\alpha$ is different between the $Si(N_3)_4$ and $Si(N_3)_6^{2-}$ molecules. The obtained results indicate that pure electronic affects might play a large role in the bonding for $C(N_3)_3^+$ and $Si(N_3)_6^{2-}$. The $Ge-N_\alpha$ bond lengths of 1.847 Å in $Ge(N_3)_4$ are shorter by 0.13 Å than those of $Ge(N_3)_6^{2-}$.[10] All $N_\alpha-N_\beta$ and $N_\beta-N_\gamma$ bond distances of the binary group 14 azides are calculated to be about 1.23 and 1.13 Å at the B3LYP level of theory, respectively, which are shorter by 0.13 Å and longer by 0.11 Å than those observed in $C(N_3)_3^+$ molecule, respectively, but very close to those of the corresponding hexaazides. The bond angles $M-N_\alpha-N_\beta$ are strongly bent at about 120.0° and show a zigzag change feature with an increase of atomic number of M (from C to Pb), as shown in Figure 2. This is due to a zigzag character of the p orbital component in constructing sp^2 hybridization orbitals of the α-N atom. With an increase of the atomic radii of M, the repulsions between valence bond orbital and lone-pair electron decrease and cause the dihedral angle of N3−N2−M1−N5 to decrease. The linear T_d symmetry $M(N_3)_4$ (M = C, Si, Ge, Sn, Pb) structures with imaginary frequencies are optimized to lie 105.6, 18.7, 38.1, 28.0, and 55.5 kcal/mol above their stable bent ones. Another completely planar D_{4h} structures are also much higher by 263.8, 79.3, 84.9, 61.5, and 89.7 kcal/mol in energy than their stable bent ones. The dissociation energy of bent $Ge(N_3)_4$ molecule for loss of one adize group is 183.6 kcal/mol.

3.2. Geometrical Structures of Binary Triazides $M(N_3)_3$. As reported in a previous paper,[5] the linear M−N−NN bond angles are not only limited to the binary group 4 tetraazides, but might also occur in other molecules, such as the binary group 3 triazides. The present calculations first showed that the binary group 3 triazides $M(N_3)_3$ (M = Sc, Y, La) are local minima without imaginary frequencies and exhibit linear structural feature at the B3LYP level of theory. For comparison, the binary group 13 azides $M(N_3)_3$ (M = B, Al, Ga, In, Tl) were also calculated at the same level. Geometrical structures of only $Sc(N_3)_3$ and $Ga(N_3)_3$ molecules are shown in Figure 1, and the other similar molecules $M(N_3)_3$ (M = Y, La; B, Al, In, Tl) are not listed again. All typical bond parameters of our calculated molecules are given in Tables 3 and 4.

The M−N−NN bond angles of $Sc(N_3)_3$ present a linear structural feature, as shown in Figure 1. Three azido groups locate symmetrically around the central atom to form a high D_{3h} symmetry $Sc(N_3)_3$ molecule. It is obvious that the $M-N_\alpha$ bond distances of 1.979, 2.154, and 2.290 Å for $Sc-N_\alpha$, $Y-N_\alpha$, and $La-N_\alpha$ are slightly longer than those of $Ti-N_\alpha$, $Zr-N_\alpha$, and $Hf-N_\alpha$, respectively, because of their different central metal atomic radii.[26] The $N_\alpha-N_\beta$ and $N_\beta-N_\gamma$ bond lengths of 1.21 and 1.14 Å are almost the same as those of the binary group 4 tetraazides, which indicate that different central metal atoms have almost no influence on the azido groups. The bond angles $M-N_\alpha-N_\beta$ and dihedral angles $M-N_\alpha-N_\beta-N_\gamma$ are both 180.0°, thus making these triazides molecules to exhibit unique linear geometrical structure. Our attempts to obtain bent $Sc(N_3)_3$, $Y(N_3)_3$, and $La(N_3)_3$ structures finally collapse into the stable linear ones, and their single-point calculations point out that they are found to be higher in energy than their stable linear ones by 38.1, 35.9, and 43.3 kcal/mol. Considering transition metal azides might possess low-lying excited states, the triplet structures are calculated to lie 72.6, 77.2, and 86.8 kcal/mol above their singlet ground states. The dissociation energy of linear $Sc(N_3)_3$ molecule for loss of one azide group is 184.5 kcal/mol and indicates a strongly endothermic reaction.

Although boron triazides $B(N_3)_3$ were reported to be shock sensitive and its calculated structure and gas-phase synthesis have already been known, it has not yet been characterized in the condensed phase.[14,17] In the present paper, the binary group 13 triazides in C_{3h} symmetry are shown to have planar pinwheel structures with the azido groups arrayed symmetrically about the central atom, as previously reported for $B(N_3)_3$ molecule.[17] The dipole moments of these molecules are almost zero. With an increase of atomic number of M, the $M-N_\alpha$ bond distances increase from B to Tl. The bond angles $B-N_\alpha-N_\beta$ of 121.6°, $N_\alpha-N_\beta-N_\gamma$ of 180.0° and the bond lengths $N_\alpha-N_\beta$ of 1.233 Å, $N_\beta-N_\gamma$ of 1.126 Å in the $B(N_3)_3$ molecule here are very close to the previously calculated values by the MP2 method.[17] The $Al-N_\alpha$ bond distances of 1.772 Å are slightly shorter by 0.07 Å than those of linear AlN_3 molecule.[27] More azido groups may make the interaction between Al and N_α stronger and the $Al-N_\alpha$ bond shorter. The bond angles $M-N_\alpha-N_\beta$ should be very close to 120.0° and show a similar zigzag change feature with an increase of atomic number of M, as shown in Figure 2. It is explained by the fact that the component of p orbitals in sp^2 hybridization orbitals of α-N atom exhibits a zigzag character. The optimizations of linear $M(N_3)_3$ (M = B, Ga, In,

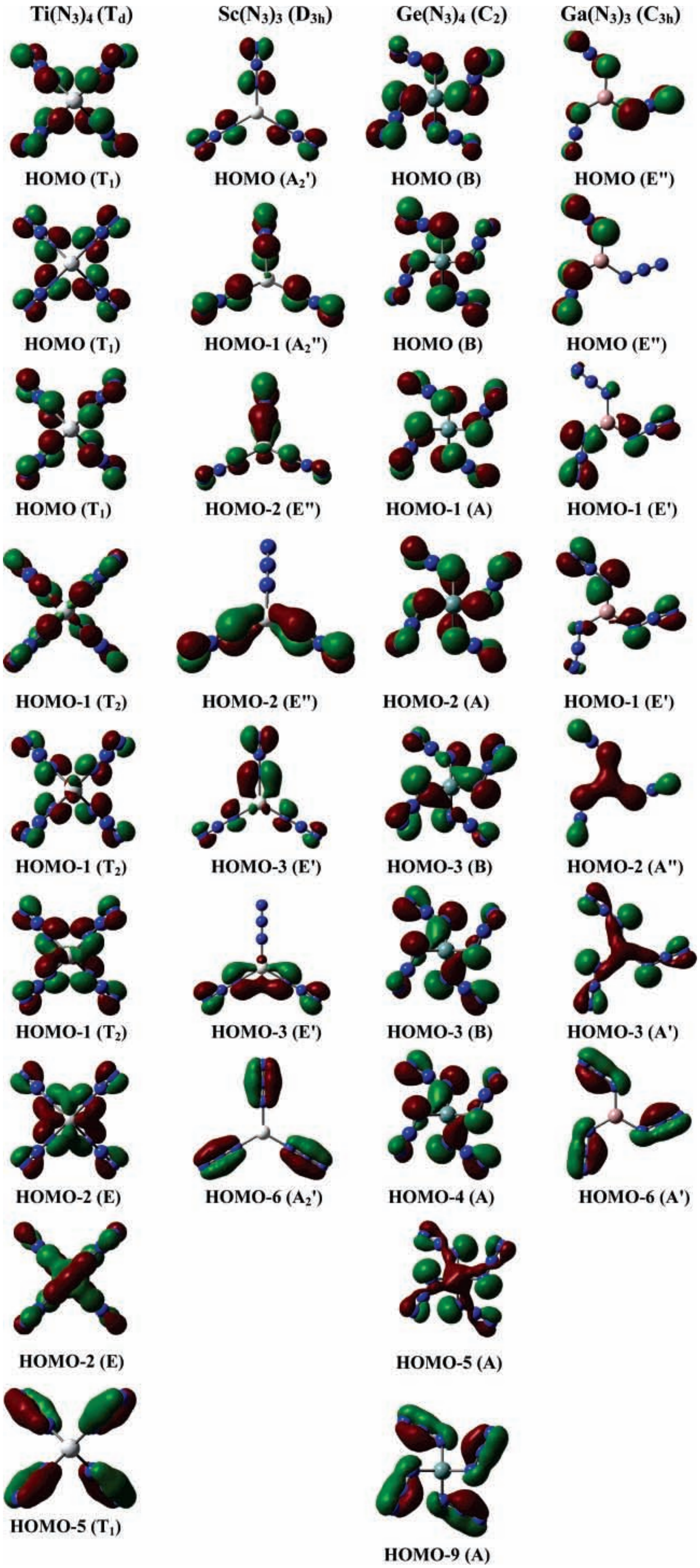

Figure 3. Molecular orbital pictures of four typical binary azides $Ti(N_3)_4$, $Ge(N_3)_4$, $Sc(N_3)_3$, and $Ga(N_3)_3$.

TABLE 3: Bond Parameters for $M(N_3)_3$ (M = Sc, Y, La) Species at the B3LYP Level of Theory

	$Sc(N_3)_3$	$Y(N_3)_3$	$La(N_3)_3$
M1−N2	1.979	2.154	2.290
N2−N5	1.208	1.208	1.211
N5−N6	1.138	1.139	1.140
M1−N2−N5	180.0	180.0	180.0
N2−M1−N3−N4	180.0	180.0	180.0

TABLE 4: Bond Parameters for $M(N_3)_3$ (M = B, Al, Ga, In, Tl) Species at the B3LYP Level of Theory

	$B(N_3)_3$	$Al(N_3)_3$	$Ga(N_3)_3$	$In(N_3)_3$	$Tl(N_3)_3$
M1-N2	1.441	1.772	1.846	1.994	2.105
N2−N5	1.233	1.214	1.228	1.218	1.228
N5−N6	1.126	1.133	1.132	1.135	1.136
N2−M1−N3−N4	180.0	180.0	180.0	180.0	180.0

Tl) structures all collapse into their stable bent ones; the single-point calculations for the former show that their energies lie 243.6, 46.4, 37.2, and 70.7 kcal/mol above the latter ones. But the optimized linear $Al(N_3)_3$ structure is only higher by 3.1 kcal/mol in energy than its bent one. The dissociation energy for loss of one azide group of bent $Ga(N_3)_3$ molecule is very high (208.9 kcal/mol), and its dissociation reaction is also strongly endothermic.

3.3. NBO Analysis of Binary Azides $M(N_3)_3$ and $M(N_3)_4$. To better explain the different geometrical structures between the group 3, 4 and group 13, 14 binary azides, a detailed NBO analysis of four typical molecules $M(N_3)_4$ (M = Ti and Ge) and $M(N_3)_3$ (M = Sc and Ga) is performed, and their molecular orbital pictures made using the GVIEW3.07 program are shown in Figure 3. The molecular orbital pictures of the other same group binary azides are not given again because of their similar molecular orbitals in nature and only slight difference in the s and p or d component of the hybridization valence orbitals. In some previous papers, the linear Ti−N−NN bond angles of the binary group 4 azides $Ti(N_3)_4$ were explained by Ti−N−N−N conjugation[4] and a nearly ideal overlap between the three valence electron pairs on the α-N atoms of the azides ligands and the three lobes of the empty d orbitals of the central atom.[5] However, some main-group binary azides, such as $B(N_3)_3$, are well-known to have bent M−N−NN bond angles, but not explained in theory.[17]

As shown in Figure 3, three degenerate HOMOs in $Ti(N_3)_4$ are a set of nonbonding orbitals occupied by the α- and γ-N atomic lone-pair electrons. The NBO analysis also shows that there are only lone-pair electrons occupied on the p orbitals of the α- and γ-N atoms yet no lone-pair electrons on those of the β-N atoms. $HOMO_{-1}$ represents a set of antibonding orbitals. $HOMO_{-2}$ is a set of π-bond orbitals largely responsible for the coordinate bonding between the central atom and the vicinal α-N atoms. The covalent π bonds arise from the interactions between two lone-pair electrons and two empty d orbitals of the central transition metal atom and between a pair of valence bonding electrons on the α-N atoms and sd^3 hybridization orbitals of the central transition metal atom. This is obviously different from three valence electron pairs of the α-N atoms donating equally into the d orbitals of the central atom, as mentioned in a previous paper.[5] $HOMO_{-5}$ is mainly responsible for the chemical bonding between each two nitrogen atoms of the azido groups.

Similar electronic density overlap is also shown in the $Sc(N_3)_3$ molecule in Figure 3. The $Sc(N_3)_3$ molecule also has similar nonbonding orbitals HOMO and $HOMO_{-1}$. The sd^2 hybridization central atom makes the $Sc(N_3)_3$ molecule exhibit triangular structural character. $HOMO_{-2}$ and $HOMO_{-3}$ represent some π bond orbitals contribution from the electron density overlap between some valence orbitals of the central atom and the α-N atoms. The α-N atoms as a donor can give two lone-pair electrons to the unoccupied d orbitals of the central Sc atom to make the $Sc(N_3)_3$ molecule to have a linear Sc−N−NN structure. NBO analysis also show that the lone-pair electrons of the α-N atoms shift toward the central Sc atom. $HOMO_{-6}$ is mainly responsible for the chemical bonding between each two nitrogen atoms of the azido groups. This gives evidence of an N−N−N conjugation to explain clearly the linear azido groups. As reported in the literature,[28] the covalent bond of a transition metal compound arises from the interactions between doubly occupied orbitals of the ligand and empty orbitals of the transition metal. Similarly, in the binary group 3 and 4 azides, the interactions between two lone-pair electrons on the sp hybridization orbitals of α-N atoms and the empty d orbitals of the central transition metal atom and a pair of valence bonding electrons density overlap result in the α-N atoms acting as a tridentate ligand and cause these compounds to exhibit a unique linear M−N−NN structural character.

We have known that the binary group 13 and 14 azides normally present bent M−N−NN structures, which is different from the linear binary group 3 and 4 azides. Their highest occupied molecular orbitals (HOMOs) of the molecules $Ge(N_3)_4$ and $Ga(N_3)_3$ shown in Figure 3 are both nonbonding orbitals occupied by the lone-pair electrons of the nitrogen atoms. $HOMO_{-1}$ and $HOMO_{-2}$ for $Ge(N_3)_4$ and $HOMO_{-1}$ for $Ga(N_3)_3$ represent some antibonding orbitals. There is only a pair of valence bonding electron density overlap between the sp^3 (sp^2) hybridization valence orbitals of the central atom and the sp^2 hybridization α-N atoms, as seen from $HOMO_{-4}$ for $Ge(N_3)_4$ and $HOMO_{-2}$ for $Ga(N_3)_3$, which is mainly responsible for the bent M−N−NN bond angles. The NBO analysis also shows more electron density occupation on the α-N atoms in the group 13 and 14 binary azides than in the group 3 and 4 ones. $HOMO_{-5}$ for $Ge(N_3)_4$ represents an antibonding orbital with a nodal surface of electronic density overlap between each two nitrogen atoms in the azido groups. $HOMO_{-9}$ for $Ge(N_3)_4$ and $HOMO_{-6}$ for $Ga(N_3)_3$ make contribution to the linear N−N−N structure of azido groups. It is obvious that the valence orbitals of main-group elements are s and p orbitals, as reported in the literature.[28] The sp^2 hybridization α-N atoms in the group 13 and 14 binary azides act virtually as monodentate donors with only one pair of valence bonding electrons to the center atom hybridization orbitals and two sterically active free lone-pair electrons still on the α-N atoms and thus result in strongly bent M−N−NN bond angles.

4. Summary

In the present paper, a series of group 3, 4 and group 13, 14 binary azides are investigated at the B3LYP level of theory. According to our calculations, they exhibit different structural character, that is, a unique linear structure in the transition metal binary azides and a normal bent M−N−NN bond angles for the main-group binary azides. The linear binary group 3 triazide molecules $M(N_3)_3$ (M = Sc, Y, La) are first reported. The NBO analysis shows that the valence orbitals of the transition metal are s and d orbitals, and those of the main-group elements are s and p functions. Different electronic density overlap between the central atom and the α-N atoms results in their remarkable different geometric structures. The α-N atoms act as a tridentate ligand in the group 3 and 4 binary azides, and those of the binary group 13 and 14 azides only give one valence electron to form one valence bonding electron pair.

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References and Notes

(1) Klapötke, T. M.; Krumm, B.; Mayer, P.; Schwab, I. *Angew. Chem., Int. Ed.* **2003**, *42*, 5843−5846.

(2) Haiges, R.; Boatz, J. A.; Vij, A.; Gerken, M.; Schneider, S.; Schroer, T.; Christe, K. O. *Angew. Chem., Int. Ed.* **2003**, *42*, 5847−5851.

(3) Knapp, C.; Passmore, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 4834−4836.

(4) Gagliardi, L.; Pyykkö, P. *Inorg. Chem.* **2003**, *42*, 3074−3078.

(5) Haiges, R.; Boatz, J. A.; Schneider, S.; Schroer, T.; Yousufuddin, M.; Christe, K. O. *Angew. Chem., Int. Ed.* **2004**, *43*, 3148−3152.

(6) Petrie, M. A.; Sheehy, J. A.; Boatz, J. A.; Rasul, G.; Surya Prakash, G. K.; Olah, G. A.; Christe, K. O. *J. Am. Chem. Soc.* **1997**, *119*, 8802−8808.

(7) Filippou, A. C.; Portius, P.; Schnakenburg, G. *J. Am. Chem. Soc.* **2002**, *124*, 12396−12397.

(8) Zigler, S. S.; Haller, K. J.; West, R.; Gordon, M. S. *Organometallics* **1989**, *8*, 1656.

(9) Denk, M.; Hayashi, R. K.; West, R. *J. Am. Chem. Soc.* **1994**, *116*, 10813.

(10) Filippou, A. C.; Portius, P.; Neumann, D. U.; Wehrstedt, K. D. *Angew. Chem., Int. Ed.* **2000**, *39*, 4333−4336.

(11) Fenske, D.; Dörner, H. D.; Dehnicke, K. *Z. Naturforsch. B* **1983**, *38*, 1301−1303.

(12) Polborn, K.; Leidl, E.; Beck, W. *Z. Naturforsch. B* **1988**, *43*, 1206−1208.

(13) Wiberg, E.; Michaud, H. *Z. Naturforsch.* **1954**, *B9*, 500.

(14) Al-Jihad, I. A.; Liu, B.; Linnen, C. J.; Gilbert, J. V. *J. Phys. Chem. A* **1998**, *102*, 6220−6226.

(15) Müller, J. *Coord. Chem. Rev.* **2002**, 1−15.

(16) Fraenk, W.; Habereder, T.; Hammerl, A.; Klapötke, T. M.; Krumm, B.; Mayer, P.; Nöth, H.; Warchhold, M. *Inorg. Chem.* **2001**, *40*, 1334−1340.

(17) Mulinax, R. L.; Okin, G. S.; Coombe, R. D. *J. Phys. Chem.* **1995**, *99*, 6294−6300.

(18) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372.

(19) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(20) Binkley, J. S.; Pople, J. A. *Int. J. Quantum Chem.* **1975**, *9*, 229.

(21) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab initio Molecular Orbital Theory*; Wiley: New York, 1986.

(22) Institut für Theoretische Chemie, Universität Stuttgart. ECPs and corresponding valence basis sets. http://www.theochem.uni-stuttgart.de/.

(23) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154.

(24) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523.

(25) Frish, M. J.; et al. *GAUSSIAN B.04*; Gaussian, Inc.: Pittsburgh, PA, 2003.

(26) http://liuyifeng.nease.net/table/etable.htm.

(27) Boo, B. H.; Liu, Z. Y. *J. Phys. Chem. A* **1999**, *103*, 1250−1254.

(28) Frenking, G.; Fröhlich, N. *Chem. Rev.* **2000**, *100*, 717.