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Study on the reaction of trimethylaluminum dimer and ammonia based on density functional theory

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ABSTRACT

AlN is prepared through the reaction of trimethylaluminum and ammonia by MOCVD. This study investigated the stable configurations of trimethylaluminum, and provided their primary bond lengths and bond angles. The reaction between the most stable configuration of TMA(C_{2v}) dimer and NH_3, was investigated, with the detailed reaction process provided. Further, a complex TMA:NH_3 and a monomer of TMA were produced. The electronic structure and some optical properties of TMA:NH_3, such as the density of states, Mulliken charge, bond population, band gap, absorption and reflectivity spectra, were further investigated. The results offer theoretical data for the application of the material TMA:NH_3.

1. Introduction

During the preparation process of aluminum nitride (AlN) by metal organic chemical vapor deposition (MOCVD), in most cases, trimethylaluminum ($Al(CH_3)_3$, TMA, or TMAl) and ammonia (NH_3) are used as precursors for Al and N, respectively [1–3]. Here a stoichiometric equation between $Al(CH_3)_3$ and NH_3 has been used:

$$Al(CH_3)_3(g) + NH_3(g) \rightarrow AlN(s)\downarrow + 3CH_4(g) \quad (1)$$

TMA is a metal-organic compound that appears as a colorless and transparent liquid state under room temperature and atmospheric pressure. A crystal structure determined in 1953 ascertained the methyl-bridged nature of $Al_2(CH_3)_6$ as one of the first examples of a metal alkyl species containing both terminal and bridging methyl groups. Then, TMA monomers were known to form stable $Al_2(CH_3)_6$ dimers which had a four-membered ring stabilized by intermolecular C—Al interaction. While trimethylaluminum is in an equilibrium between the monomeric and dimeric species in the gas phase, the dimeric $Al_2(CH_3)_6$ appears to be the sole form of occurrence in condensed phases [4].

The dimeric TMA (d-TMA) was a spatial structure with a four-membered ring (Al—C—Al—C), and six carbon atoms were in two nearly perpendicular planes. Two monomers were connected by two three-center–two-electron bridging bonds [5]. It can be explained as follows: The aluminum atoms form four sp^3 hybrid orbitals in dimers. One aluminum atom has three valence electrons, of which two valence electrons form two normal terminal C—Al bonds, respectively. There is only one valence electron in the other two orbits. Meanwhile, the methyl carbon atoms at the bridge are also sp^3 hybrid. Each atom has four valence electrons, of which three orbitals form normal C—H bonds. The remaining one forms bridging bonds with two Al atoms. There are three atoms (Al—C—Al) in the bridging orbital, that is, the three centers, but there are only two electrons with opposite spin. Therefore, the bridging bonds are called three-center–two-electron bonds. The bridge is electron deficient, so the bond lengths are longer than those of the normal C—Al bonds.

By simulating calculation of the dissociation-association equilibrium of dimer and monomer of trimethylaluminum in gas phase, Wu et al. [6] found that a C_{2v}-like dimeric geometry was lower energy structure.

The reaction between monomeric TMA (m-TMA) and ammonia has been reported by many studies, with $Al(CH_3)_3$:NH_3 (TMA:NH_3) as the well-recognized product [7–9]. However, few studies have been performed on the reaction of TMA dimer and ammonia. The reaction was just briefly mentioned in Ref. [10], in which two $Al(CH_3)_3$ molecules were first polymerized into a stable $Al_2(CH_3)_6$ dimer, which was then dissociated immediately to two monomers as an ammonia molecule approached, and then one of them made the complex TMA:NH_3; however, no explicit explanations were given.

This study aims at revealing the detailed reaction process of TMA (especially TMA dimer) and NH_3, as well as the electronic structure and

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some optical properties of product TMA:NH_3.

2. Calculation methods and models

2.1. Calculation methods

All calculations were performed by the CASTEP module of the Materials Studio software based on density functional theory. Ultrasoft pseudo-potentials were used to describe the interactions between nuclei, inner electrons, and outer electrons in the system. The valence electrons of the primary atoms were Al-$3s^2 3p^1$, N-$2s^2 2p^3$, C-$2s^2 2p^2$, and H-$1s^1$. The exchange-correlation potential of the interactions between the electrons were expressed as the PW91 form from the generalized gradient approximation (GGA) representation and calculated using the BFGS algorithm. The plane wave cut-off energy was defined at E_{cut} = 300 eV, and the Brillouin zone k-point was defined at the gamma point, i.e., 1 × 1 × 1. Whether spin polarization or non-spin polarization was performed as geometric optimization, the results were the same. The iterative convergence criteria were set with the energy convergence value of 2.0×10^{-5} eV/atom, the maximum force of 0.05 eV/Å, the maximum stress of 0.1 GPa and the maximum displacement of 0.002 Å.

2.2. TMA stable configurations

Several configurations of the TMA were constructed and geometrically optimized, and three stable configurations were obtained: a monomer and two configurations of dimer (see Fig. 1). The monomer of TMA was trigonal-planar symmetric gyroscope, belonging to C_{3h} group. And it would become slightly pyramidal when involved in the complex.

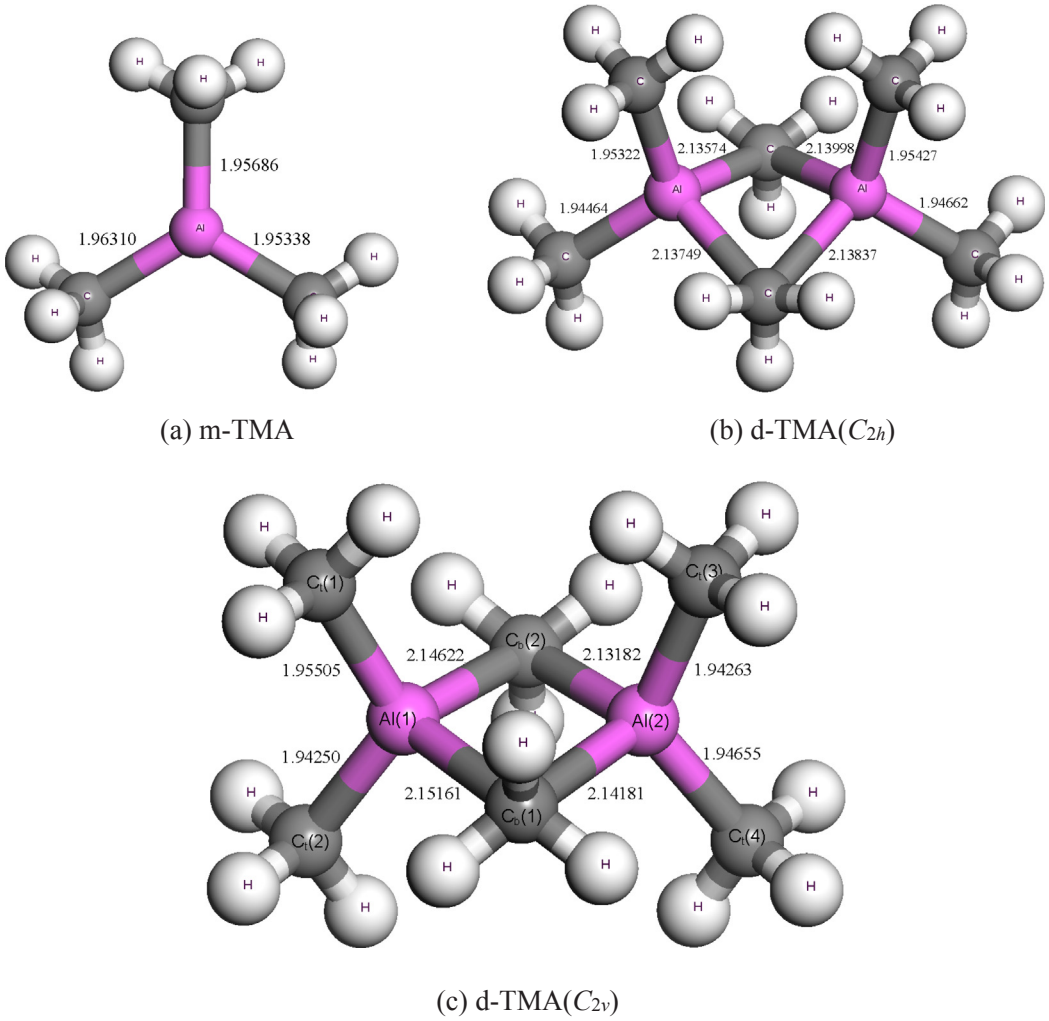
Table 1
TMA energy.

Stable configuration	Energy ($\times 10^3$ eV)
m-TMA	−0.66803
d-TMA(C_{2h})	−1.33733
d-TMA(C_{2v})	−1.33744

There were two dimeric configurations, namely C_{2h} and C_{2v}. They both had a four-membered ring with two bridging methyl groups and were asymmetric gyroscope. The difference was slight only with different positions of hydrogen atom in the bridging methyl.

Seen from Table 1, d-TMA(C_{2v}) was the most stable configuration, as it had the lowest energy, which was also less than twice the energy of the m-TMA. The C—Al bond lengths and primary bond angles are indicated in Fig. 1 and Table 2, with the terminal carbon atom represented by C_t, and the bridging methyl carbon atom represented by C_b in d-TMA(C_{2v}).

As shown in Table 2, the geometric parameters were similar to those from Refs. [4,11]. Among these results, we found that d-TMA(C_{2v}) had an average bond length of C_b—Al = 2.14287 Å, longer than the average



(a) m-TMA (b) d-TMA(C_{2h})

(c) d-TMA(C_{2v})

Fig. 1. TMA stable configurations (Bond lengths in Å).