

Calculation of the relative stability of molecular alumoxanes

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Abstract

Calculations have been performed on a series of alumoxane rings and cages having the formula $[\text{HAlO}]_n$ ($n = 2\text{--}10$). Results from these calculations are in excellent agreement with previous calculations on methyl alumoxane rings and cages and experimental structures of organic alumoxane rings and cages. Optimized aluminum–oxygen bond lengths of both rings and cages were found to increase with decreasing stability of these compounds. Comparison of the calculated IR spectra for all of these cages with the experimental spectra of methyl alumoxane (MAO) catalyst suggests that the structure of MAO is composed of large cages containing both four- and six-membered rings.

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1. Introduction

For over 45 years, it has been known that alkyl-substituted alumoxanes can function as catalysts [1,2]. In 1980, Sinn and coworkers demonstrated that methylalumoxane (MAO) can function as a co-catalyst with group 4 metallocenes in alkene polymerization reactions [3,4]. While the structure of the methylalumoxane catalyst remains unknown, experimental and theoretical investigations have provided a number of significant insights into this problem. While it was thought initially that the structure of methylalumoxane was composed of linear chains or rings, based in part on the crystal structure [5] determined for the $[\text{Al}_7\text{O}_6\text{Me}_{16}]^{-1}$ anion, it is now accepted that three-dimensional cage structures are more likely based on experimental observations and theoretical calculations. For example, analysis of ^{27}Al NMR spectroscopic measurements on MAO [6,7] indicates that these structures contain predominantly four-coordinate aluminum atoms and three-coordinate oxygen. In 1993, Barron and coworkers published the first crystal structures of alkylalumoxanes [8], giving details

for rings and cages containing three, four, and six aluminum atoms. The following year, this group published [9] the crystal structure of a cage containing eight aluminum atoms.

A wide range of theoretical investigations on alumoxanes have been reported, and a review of these has recently appeared [10]. Many of these theoretical investigations have been closely tied to experimental studies. For example, experimental ^{27}Al NMR parameters obtained from samples of pure MAO have been compared with parameters derived from molecular orbital calculations on proposed structures [11] to test these structural models. In another study [12], experimental ^1H and ^{13}C data obtained for MAO and molecular analogs in the presence of dimethylzirconocene were compared with a range of model compounds to predict both the most likely structures of active and dormant species, and to also predict the ideal Al/Zr ratios.

A range of structural models for MAO have been considered. Theoretical investigations on rings and cages having the general formula $[\text{RAIO}]_n$ have uniformly concluded that cage structures are more stable than ring or chain isomers [13–15]. While the formula $[\text{RAIO}]_n$ appears ideal from a valence-charge perspective and corresponds to several structurally characterized molecules, it has been noted

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that the typical MAO catalyst has a Me/Al ratio around 1.5:1. Examination of the IR spectrum of MAO shows a band at 1257 cm^{-1} , which has been assigned [16] to bridging methyl groups (Al–C–Al). Studies on well-characterized molecular compounds have given insight into this process. It has been reported [17] that reaction of $[(^t\text{Bu})\text{Al}(\mu_3\text{-O})_6]$ with trimethylaluminum (TMA) proceeds to give two closely related structures, characterized by ^1H and ^{13}C NMR, which both contain bridging methyl groups. A number of theoretical investigations have been reported [18–20] examining potential structures and pathways for opening of $[\text{RAIO}]_n$ cages with TMA to obtain both terminal and bridging methyl groups.

While much effort has gone toward determining the structure of MAO, workers are also using these investigations to potentially develop new catalytic systems. Alumoxanes are generally prepared by controlled hydrolysis of aluminum alkyls or organoaluminum hydrides. Compounds containing terminal aluminum-bound OH groups have long been considered intermediates in these reactions, but have been difficult to isolate. Recently, a number of mono- and di-nuclear aluminum compounds have been isolated and characterized [21,22]. While mono- and di-aluminum molecules are not realistic models for MAO, it has been demonstrated that these compounds react with dimethylzirconocene (Cp_2ZrMe_2) to form compounds that exhibit catalytic activity for ethylene polymerization that is higher than observed for MAO [23].

The goal of the present study is to analyze trends in $[\text{AlO}]_n$ rings and cages to determine patterns that can be used to guide characterization of more complex structures. While the relative stability of most of the compounds included in the present study (or closely related analogues) have previously been published, calculated vibrational data has not been reported for most of these compounds. By comparison of the closely related series of compounds included in this study at a uniform level of theory, it should be possible to clearly observe trends which could have implications for experimental workers.

Schaefer et al. [24] have demonstrated that the $[\text{AlO}]_4$ core is insensitive to the choice of ligand for the heterocubane. For this reason, calculations were performed on a series of $[\text{HAIO}]_n$ rings and cages instead of the more computationally demanding alkylalumoxanes. The structures of the molecules studied in this investigation are shown in Figs. 1 and 2. All of these compounds have the general formula $[\text{HAIO}]_n$, are electrically neutral, and can be divided into two groups. The cyclic or ring compounds contain three-coordinate aluminum atoms and two-coordinate oxygen atoms. The cage compounds contain four-coordinate aluminum atoms and three-coordinate oxygen atoms. Finally, three different computational procedures were used in this investigation in order to evaluate trends and determine which level of theory is most appropriate for studying these types of molecules.

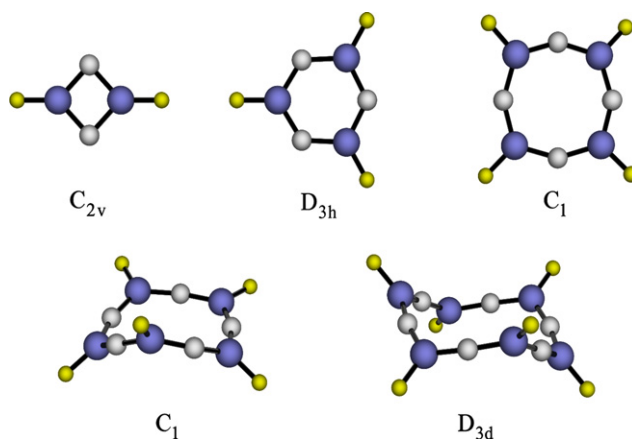


Fig. 1. Optimized geometries of $[\text{HAIO}]_n$ rings.

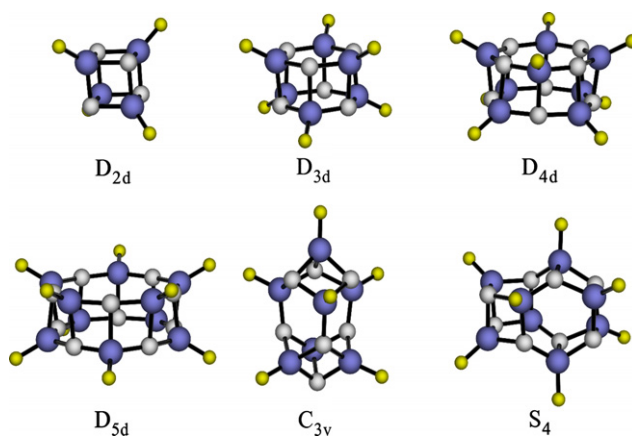


Fig. 2. Optimized geometries of $[\text{HAIO}]_n$ cages.

2. Computational methodology

All calculations were performed using the GAMESS [25] program on personal computers running under a Linux operating system. For all calculations, the 6-31G(d) basis set was used, and were performed using direct SCF procedures [26,27]. Molecular geometries were fully optimized within the indicated symmetry constraints using Baker's method [28]. For RHF calculations, the default convergence criteria was used, which requires that both the maximum and RMS gradient components be less than 10^{-4} and $\frac{1}{3} \times 10^{-4}$, respectively. For DFT calculations, both the gradient-corrected exchange functional of Becke [29] and the non-local, hybrid exchange functional B3LYP were used. The parameters for the numerical grid were $\text{NRAD} = 96$ (radial grids), $\text{NTHE} = 36$ (angle θ grids), and $\text{NPHI} = 72$ (angle ϕ grids).

Force calculations were performed to characterize the stationary points obtained, using the same level of theory and identical basis sets for all optimized geometries. In all cases, the Hessian matrices were positive definite, which verified that these optimizations had converged to local minima on the potential energy surface. The total energies reported do not include in any corrections for zero-point

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