

Uncovering the Chirality of Triazasumanene

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Abstract

Few heteroatom-doped buckybowls have been synthesized and thoroughly studied for rational design of the next generations of buckybowls. This may be attributed to the difficulty of synthesizing buckybowls and understanding the stabilities of these structures. The chirality of triazasumanene is investigated to understand the overall energetics and to provide an avenue for the possibility of combining computational and experimental work to synthesize the next generation of heteroatom-doped sumanene. A theoretical study was launched performing geometry ground state optimization, transition state optimization, and circular dichroism spectrum.

1 Introduction

Miniaturization of novel devices and machines on a molecular level has been one of the main goals in electronics[1]. The decreasing device size may lead to greater power and functionality residing on a chip. For instance, polycyclic aromatic carbons with curved π -conjugated structures, such as fullerenes, carbon nanotubes, and buckybowls are appealing materials due to their low density, structural stability, and extended-delocalized π networks that support mobile charge carriers[2]. However, few heteroatom-doped buckybowls have been synthesized and reported. The most recent successful synthesis of triazasumanene is an isoelectronic heteroanalogue of sumanene from Tan et. al.[3]

First principle calculations may provide insights on the electronic structures of these sumanene derivatives and improve upon the current state-of-the-art. In this report, we provide a theoretical investigation of the triazasumanene by computing the optimized ground state and transition state structures with the corresponding electronic circular dichroism (ECD) that may lead to further joint computational and experimental studies.

2 Methods

2.1 Statement of the Models

A racemic mixture is a 50:50 mixture of two enantiomers. In the synthesis of triazasumanene, two absolute stereochemical configurations coexist which are designated as

clockwise (C) and counterclockwise (A) as shown in Fig 1. The configuration is based on the heteroatoms having the lowest possible number.

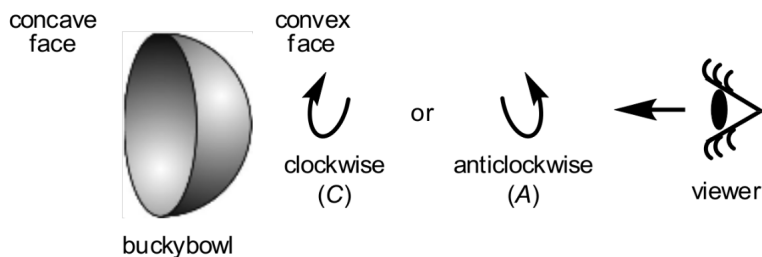


Figure 1: An illustration demonstrating the nomenclature of buckybowl enantiomers.

To resolve the racemic triazasumanene, one method is to use electronic circular dichroism (ECD) spectroscopy coupled with electronic structure calculations.

2.2 Computational Details

Within the TURBOMOLE v7.2 suite[4], the aoforce and escf module are used to compute the vibrational frequencies and generate the ECD spectrum. The triazasumanene structure was constructed on avogadro v1.2[5] and minimized with universal force field (UFF). This initial structure was fairly planar and this initial guess was used to optimize with TPSS[6] using def2-SV(P) basis and D3 dispersion correction[7]. A total of three transition states were optimized from the structure built in avogadro. Two of the transition states were constrained with C_{3h} symmetry while the third was constrained with C_3 symmetry.

3 Results

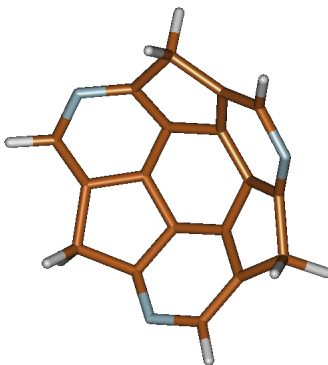


Figure 2: The optimized ground state configuration of (C)-triazasumanene using TPSS functional with def2-SV(P) basis set.

Triazsumanene was successfully optimized falling toward the (A) configuration verified through harmonic vibrational analysis and revealing a C_3 point group symmetry as seen in Fig 2. Following the ground state optimization, a transition state search was performed and a total of three transition states were found. The starting geometry was generated from avogadro v1.2[5] with a fairly planar structure. The C_{3h} constrained optimization lead to a structure that breaks C-C bonds while the C_3 constraint maintained the planarity of the ring structures (Fig 3).

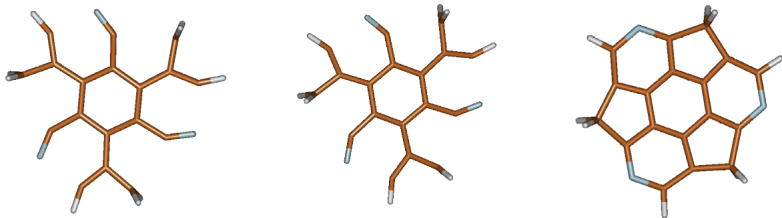


Figure 3: Symmetry constrained optimized structures of three transition states where the C_{3h} symmetry (left and middle) and C_3 symmetry (right) were applied. The structures are labeled from left to right as transition states 1, 2, and 3.

A closer look at the free energies of the transition states reveal that the optimized transition state constrained with C_3 symmetry has a closer racemization energy to the experimental result of 38.2 kcal/mol at 476K[3]. This may be attributed to the broken C-C bonds seen in the C_{3h} symmetry constrained optimization (Tab ??). In addition, the harmonic vibrational analysis of the transition state structures revealed that the C_3 symmetry constrained transition state is verified to be a transition state due to having only 1 imaginary frequency.

Table 1: The transition state free energies computed with TPSS-D3 and def2-SV(P) basis set. Transition states 1 and 2 were constrained with C_{3h} symmetry while transition state was constrained with C_3 symmetry. Racemization barrier is computed by taking the difference in free energy between the ground state and transition state. The total free energy of the ground state is -5.3649E5 kcal/mol.

Transition State	Total Free Energy (kcal/mol)	Racemization Barrier (kcal/mol)
1	-5.3621E5	279.25
2	-5.3623E5	262.55
3	-5.3645E5	40.85

Lastly, the CD spectrums of both absolute configurations (A)- and (C)-triazasumanene were computed and the spectrums reveal unique rotary strength at different wavelengths (Fig 4 and 5).

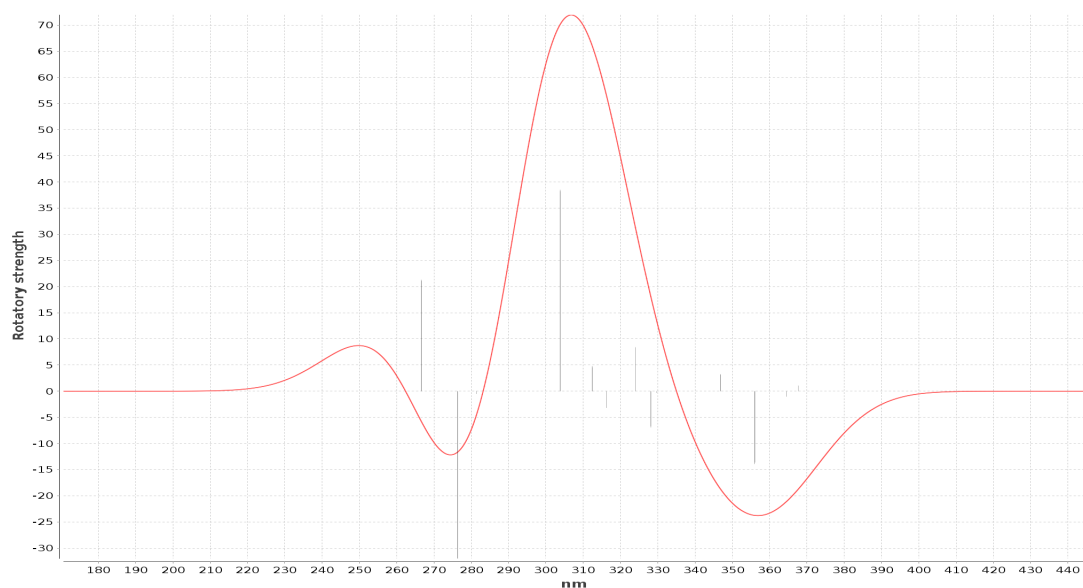


Figure 4: This is a computed CD spectrum of the ground state (A)-triazasumanene for the first 20 dipole allowed excitations and broadened rotary strengths with Gaussians using 0.16 eV linewidth.

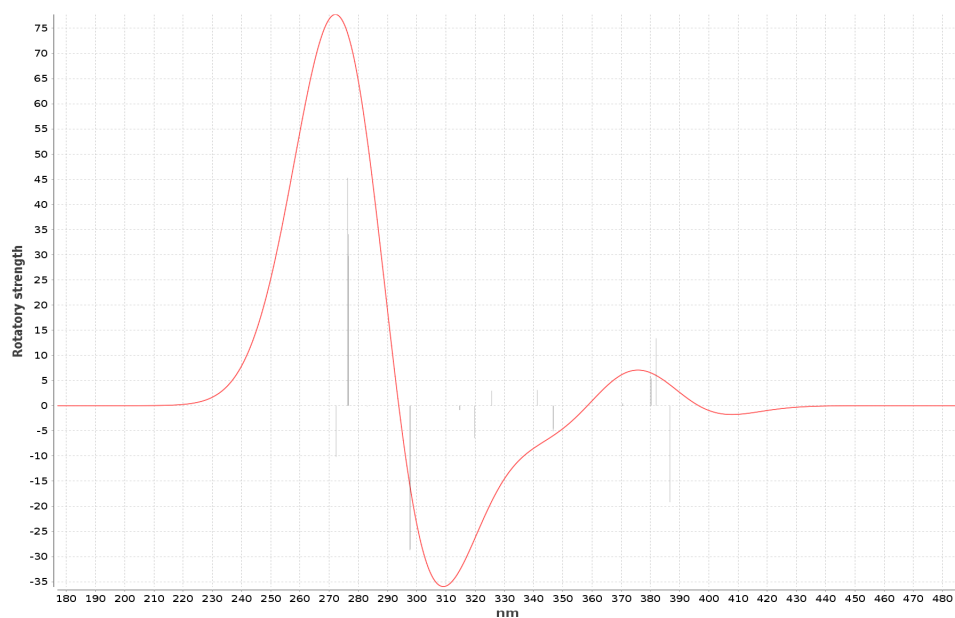


Figure 5: The CD spectrum of (C)-triazasumanene for the first 20 dipole allowed excitations and broadened rotary strengths with Gaussians using 0.16 eV linewidth.

4 Conclusions

In summary, the elucidation of the chirality of triazasumanene can be achieved through computation as seen by the free energy calculations and computed CD spectrum of both absolute configurations (A) and (C). Three transition states were found and it was discovered that only the C_3 symmetry constrained transition state was valid. Moreover, the computed CD spectrum was fairly close to experimental CD spectra[3] for the excitation at around 272 nm. However, the lower excitations did not align with the experimental CD spectra[3]. The work presented provides a baseline for future improvement to computational studies of triazasumanene.

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