Experiment 51

1,3-Di-1-adamantylimidazol-2-ylidene. A Stable Singlet Carbene

*Semi-empirical AM1 calculations are used to characterize the title molecule and to compare it to the analogous 1,3-dimethyl derivative. The energetics of CH bond insertion is calculated, and used to rationalize the title molecule's stability.*

Carbenes are highly-reactive species that rapidly undergo several types of reactions, including cycloaddition with alkenes and insertion into alkane CH bonds. The title molecule, 1A, is exceptional, however, in that it forms a stable solid, the structure of which has been determined by X-ray crystallography.¹

![Chemical Structures](image)

The apparent stability of 1A raises two questions: 1) is its stability kinetic or thermodynamic? and 2) is it stabilized by steric factors (hindrance by the adamantyl groups), by electronic factors (1A contains a six electron, “aromatic”, π system), or by some combination of the two? The first question can be answered by calculating the energetics of a typical carbene reaction, such as insertion into the CH bond of CH₄, i.e.,

$$X_2C + CH_4 \rightarrow H - CX_2 - CH_3$$

“Kinetic stability” requires a larger barrier for 1A insertion than for a “normal” singlet carbene, such as CCl₂, while “thermodynamic stability” requires 1A insertion to be endothermic. The second question can be answered by comparing 1A with another carbene that shares either its steric or electronic characteristics. Since the methyl groups in 1M are substantially smaller than the adamantyl groups in 1A, these two carbones should have similar electronic properties, but very different steric properties.

In this experiment, you will use semi-empirical AM1 calculations to compare the structure and electronic properties of 1A and 1M, and to establish the energetics of the CH bond insertion reaction shown above.


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Preparation

BuOCH₃ or Me₂SO₄ can be used as the solvent for the carbene insertion reaction. The reaction is sensitive to air and moisture, so the solvent should be degassed prior to use. The reaction is carried out in the dark, and under an atmosphere of argon or nitrogen.

Soxhlet extraction is used to extract any remaining solvent from the crude reaction mixture. The solvent is then removed under vacuum.

Open*Cap

An open*Cap is used to prevent the reaction from being contaminated by moisture, oxygen, or other impurities.

Support

A support is used to hold the reaction mixture in place during the reaction. The support should be insulated from the reaction mixture to prevent contamination and to ensure that the reaction is carried out at room temperature.

Homemade*Cap

A homemade*Cap is used to hold the reaction mixture in place during the reaction. The homemade*Cap is designed to be compatible with the support and reaction mixture, and to be insulated from the reaction mixture to prevent contamination and to ensure that the reaction is carried out at room temperature.

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Procedure

Build 1A, 1M, and CCl₂, optimize their geometries using semi-empirical AM1 calculations, and record their energies. (Assume that all three carbenes are singlets.) Next, build CH₄ and the products obtained from CH insertion of each carbene. Optimize their AM1 geometries (note: stagger the ring substituents on alternate sides of the ring in the products derived from 1A and 1M), record their energies, and calculate ΔH_rxn for each insertion. Use these results to assess whether 1A is thermodynamically stable with respect to CH insertion. The AM1 barriers for CH insertion are approximately 20, 50, and 50 kcal/mol for CCl₂, 1M, and 1A, respectively. Use these results to assess whether 1A is kinetically stable with respect to CH insertion. What relationship exists between the AM1 barriers and reaction enthalpies? What do these results suggest about the relative role of steric and electronic factors in stabilizing 1A? (Assume, for the sake of argument, that 1A and 1M are electronically similar.)

Molecular models provide a better test of electronic/steric similarity than simple molecular formulas. What are the ring bond lengths in 1A and 1M? Do these imply similar π interactions in each? Compare space-filling models of the two carbenes. Do the adamantyl and methyl groups offer significantly different steric environments?

Optional

Another way to compare the electronic properties of different carbenes is to examine the shapes and energies of their reactive orbitals. A singlet carbene has two reactive orbitals, a filled σ-type orbital and an empty p-type orbital (see: Substituent Effects on Reactive Intermediates). Identify the reactive orbitals in each carbene by calculating and displaying various high-energy occupied orbitals and low-energy unoccupied orbitals. Record the energies of these orbitals and decide whether 1A and 1M are electronically similar in an “orbital” sense. How do these carbenes differ electronically from CCl₂? Which carbene is a better donor? A better acceptor? Given the relatively low barrier for CCl₂ insertion into CH bonds, what do these orbital energies suggest about the direction of electron transfer in the insertion transition state?