Computational Chemistry One: Norcamphor and Thiophene

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1 Introduction

1.1 Purpose

Determine the favored method of nuclephilic addition to norocamphor and camophor using LUMO surface maps created in Spartan Student Ver. 9. Determine the aromaticity of thiophene by comparing the energy of hydrogenation reactions calculated by comparing the structure energies calculated in Spartan Student Ver. 9.

1.2 References

Hehre, W. J.; Shusterman, A. J.; Huang, W. W. *Abstracts from: A Laboratory Book of Computational Chemistry.* Wavefunction, Inc. Irvine, CA. **1996**.

McQuarrie, D. A.; Simon, J. D. *Physical Chemistry: A Molecular Approach*; University Science Books: Sausalito, CA, **1997**.

Wiser, D.; *Conjugated Dyes: The Particle in A Box Experiment*; Lake Forest College: Lake Forest, IL, **2025**; pp 1-3.

Spartan Student Ver. 9. Wavefunction: 18401 Von Karman Ave Irvine, CA, 2025. `https://store.wavefun.com/product_p/spstudent.htm`

1.3 Safety Information

There are no safety risks associated with this experiment.

2 Methods

2.1 Norcamphor

A molecule of norcamphor and a molecule of camphor (Fig. 1) were modeled using the organic kit of the Spartan model builder. The structure was minimized using a Hartree-Fock calculation with a 6-31g* basis set. A map of the lowest unoccupied molecular orbital (LUMO) surface and a map of the electron surface density were added.
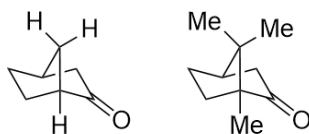

Figure 1: Chemical structures of norcamphor (left) and camphor (right)

2.2 Thiophene

Molecules of thiophene, dihydrothiophene, tetrahydrothiophene, and dihydrogen were modeled using the organic kit of the Spartan Student Verison 9 model builder. The structures were optimized using a Hartree-Fock calculation with a 6-31G* basis set. The final energy of each structure was recorded and used to calculate the overall enthalpy of a hydrogenation reaction (Fig. 2).
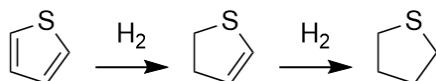

Figure 2: Hydrogenation of thiophene to dihydrothiophene to tetrahydrothiophene.

3 Results/Data

3.1 Norcamphor

The LUMO of norcamphor peaked through the electron density on either side of the carbonyl carbon. The LUMO of camphor only peaked though on the bottom of the carbon, away from the bridgehead. (Fig. 3).
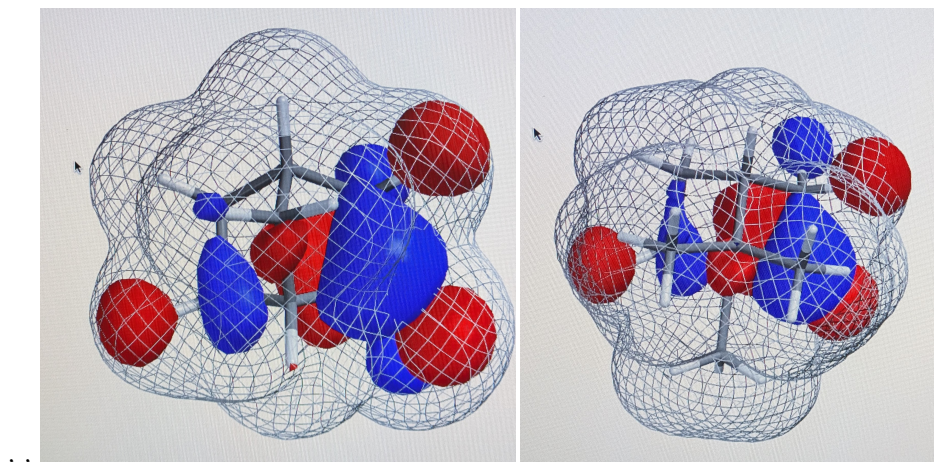

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Figure 3: An overhead view, looking down on the bridgehead carbon of norcamphor (left) and camphor (right) with an electron density surface (mesh) and a LUMO surface (solid).

3.2 Thiophene

The final optimized structures had similar energies in Hartree-Fock, so for better comparison, units of Gibb's free energy of hydrogenation (Table 1) were changed to kcal/mol using the conversion 1 HF = 627.5 kcal/mol.

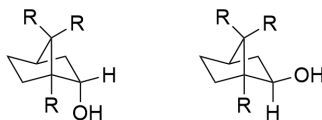**Table 1:** Energies of Thiophene structures and hydrogenation reactions

	Total Energy (HF)	Hydrogenation (kcal/mol)
Thiophene	-551.290352	-22.88
Dihydrothiophene	-552.453645	-39.99
Tetrahydrothiophene	-553.644208	-
Hydrogen	-1.126827	-

The bond lengths of thiophene were compared to the bond lengths of benzene, and aromatic compound, and *cis*-1,3 butadiene, a non aromatic compound (Fig. 4). The bond lengths of benzene were all equal length while the bond lengths of thiophene and *cis*-1,3 butadiene varied.

Figure 4: Comparison on the bond lengths (in Å) of thiophene to a non-aromtic compound, *cis*-1,3 butadiene, and an aromatic compound, benzene.

4 Conclusion

4.1 Norcamphor

Figure 5: Endo alcohol formed by an exo nucleophilic attack (left) and Exo alcohol formed by an endo nucleophilic attack (right).

The LUMO peaked out of the electron surface on the bottom of the ring, favoring an exo nucleophilic attack forming an endo alcohol product (Fig. 5), because the electron density in that region was more easily accessible. This is also supported by steric affects of the products, as the endo product has the alcohol in the more stable equatorial position.

4.2 Thiophene

The overall Gibb's free energy was calculated with the assumption $\Delta S = 0$ so $\Delta H \approx \Delta E$. Hydrogenation of thiophene was less favorable than hydrogenation of dihydrothiophene, which was an indication that thiophene was a more stable reactant and less prone to react. This suggested that thiophene could be aromatic however, the C-C bonds had more similarity with the C-C bonds in butadiene than in benzene since they varied in length. A longer C-S bond was expected however, even the C-C bonds varied in length. This provided evidence against thiophene being aromatic.