A Theoretical Study of Cyclopropane Carboxylic Acid

Rajarshi Guha (9915607)

October 3, 2002

1 Introduction

This report describes a satudy of cyclopropane carboxylic acid (CPCA) using theoretical methods. Various parameters of this molecule were evaluated including the minimum energy of the molecule (as obtained from a geometry optimization of an initial input structure), vibrational jodes and thermochemical data. In addition a comparison of basis sets and methods was made using the energy as an indicator of the effectiveness of a given basis set and/or method in describing a molecular property.

2 Procedure

The molecule was initially drawn using DTMM on Windows95. The resultant output file (which was in the CSSR format) was then converted using Babel (available at *http://chin.icm.ac.cn/software/babel.htm*) to a Gaussian z matrix format. This initial geometry in the z matrix format was then used as input to Gaussian98, with which all subsequent calculations were carried out.

The initial job was a full geometry optimization with a 6-31G basis set and a RHF method.[1–5] Using the resultant optimized z matrix (which is presented later in this report) a vibrational frequency analysis and thermochemical analysis was carried out. In addition the energy of the optimized structure was also reported - since the geometry has been optimized the energy represents the minimum energy of the molecule. Fig. 1 is an image of the optimized geometry of CPCA. Unfortunately the actual energy of the molecule (from bomb calorimetry or any other experiment) was not available for comparison. Instead a crude comparison was carried out by taking the sum of the individual bond energies of each bond present in CPCA and using that as the experimental value. A Gaussian job was carried out to evaluate electron densities as well as electrostatic potential of the molecule, again, using the optimized geometry evaluated in the first part of this study. The resultant electron density was visualized with Molekel (available at *http://www.cscs.ch/molekel/*). Using this software an electron density isosurface was generated. The electrostatic potential was mapped onto this isosurface. The resultant contour image can be seen (unfortunately in monochrome!) in Fig. 2. Molecular orbital's were also evaluated and images for the HOMO and LUMO of the molecule can be seen in Figs. 3 & 4. Finally the charges on each of the atomic centers were also evaluated and this data is represented in Fig. 5.

The above energy calculation (a.k.a Single Point energy calculation) was repeated for a variety of basis sets (keeping the method fixed) as well as with a series of methods (keeping the basis set fixed). The aim of this comparison is to show the effects of basis sets and methods on ab initio calculations using CPCA as an example case. In all cases the geometry taken was the optimized geometry obtained above.

3 Results

All results below have been evaluated using a 6-31G basis set with a RHF method using the optimized geometry unless otherwise mentioned.

3.1 Energy & Enthalpy

$$\begin{aligned} \text{Computed Energy} &= \text{-304.415035 Hartrees/particle} \\ \text{Computed Enthalpy} &= \text{-304.414091 Hartrees/particle} \\ \text{Experimental Enthalpy} &= \text{?} \end{aligned}$$

The computed energy is the sum of the electronic energy and thermal correction to energy as evaluated by the thermochemical calculation. Similarly the computed enthalpy is the sum of the electronic energy and the thermal correction to the enthalpy It should be remembered that the *experimental* value is actually a sum of the bond energies of the bonds making up the molecule and is not an experimentally evaluated enthalpy.

3.2 Dipole Moment (μ)

$$\begin{aligned} \text{Computed Dipole Moment} &= 5.5125 \text{ Debye} \\ \text{Experimental Dipole Moment} &= \text{? Debye} \end{aligned}$$

In a subsequent section we see that both the energies and dipole moments are affected by the choice of basis set for the calculation. On the other hand, change of method does not give a large variation of these values.

3.3 Comparison of Basis Sets & Methods

Below, Tables 1 & 2 represent the results of single point energy and dipole moment calculations for various combinations of basis sets and methods. Note that this energy refers to electronic energy only.

As can be seen from the above tables, for the molecule in question, the choice of basis set has a larger effect on the variation of the energy and μ values than the method involved. In Table 1 going down the table uses progressively more refined basis sets. As can be seen, the use of the STO-3G basis set (i.e. primitive Slater type orbitals) leads to a very bad value of the dipole moment. The energy obtained is also less than that obtained in other cases but the difference is not so large. In the 3-21G and the 6-21G basis sets Gaussian type orbitals are used which map more effectively to idealized atomic orbitals. The larger number of primitives taken in the 6-21G set result in more accurate values of both dipole moment and energy.

On the other hand the data in Table 2 indicates that there is not much gain in accuracy by using more sophisticated methods. The UHF and RHF methods give identical values since for the case of CPCA there are no unpaired electrons. On going to more accurate methods (viz. MP2 & MP3) we do not gain much in accuracy whereas the calculations take a longer time.

The last three methods are DFT methods. All three use the correlation functional of Lee, Parr and Yang[24,25] (the LYP part of the name). The SLYP method combines the correlation functional with a Slater exchange functional[20,21] and the BLYP method uses a Becke functional.[22] The B3LYP method is a Becke 3 parameter hybrid method. As can be seen the calculated dipole moment calculated by DFT methods does not give a good

Method	Basis Set	μ (Debyes)	Energy (Atomic Units)
RHF	STO-3G[6,7]	3.43	-300.737276839
	3-21G[8–10]	5.0581	-302.958972807
	6-31G[1–5]	5.5104	-304.524845316
	D95[11]	5.6753	-304.574059105
	D95V[11]	5.6768	-304.573203539

Table 1: Varying basis sets

Basis Set	Method	μ (Debyes)	Energy (Atomic Units)
6-31G	RHF[1–5]	5.0581	-304.524845316
	UHF	5.5104	-304.524845316
	MP2[12–15]	5.5125	-304.524849459
	MP3[16,17]	5.5125	-304.524849459
	CI[16,18,19]	5.5125	-305.05256850
	SLYP	4.7039	-302.404283609
	BLYP	4.5898	-306.256837144
	B3LYP	4.8203	-306.355436670

Table 2: Varying methods

match with that obtained by other methods (though using more sophisticated DFT methods does indicate that the value of the dipole moment can be improved).In addition, the SLYP method gives a lower energy compared to both other DFT methods as well as the other non DFT methods - mainly due to the primitive nature of the Slater functional compared to the Becke.

The conclusion from the above data is that for the given molecule (and in general for small molecules) relatively simple basis sets and methods suffice. If more accuracy is needed then using an improved basis set is preferable to using a more sophisticated method - especially when considering the computation time involved. In addition the method should be chosen keeping in mind the molecular properties to be evaluated - all methods are not good for all properties!

3.4 Thermochemistry

In this section the results of thermochemical calculations are reported. All results are at 298.15K and at 1 atm. pressure.

Zero point vibrational energy = 65.42636 Kcal/mol
Zerro point correction = 0.104264 (Hartree/particle)
Thermal correction to energy = 0.109814
Thermal correction to enthalpy = 0.110758
Thermal correction to entropy = 0.074795

Next the values of total thermal energy (E), specific heat at constant volume (C_v) and entropy (S) are tabulated. In addition contributions from electronic, rotational, translational and vibrational modes are included.

	E (Kcal/mol)	C_v (cal/mol-K)	S (cal/mol-K)
Total	68.909	19.141	75.692
Electronic	0.000	0.000	0.000
Translational	0.889	2.981	39.270
Rotational	0.889	2.981	26.294
Vibrational	67.132	13.179	10.128

As can be seen from the above data the thermal energy arises mainly from vibrational modes. The same occurs for rotational energy. For the case of entropy translational, vibrational and rotational modes all have significant conntributions.

3.5 Optimized Z Matrix

Below is presented the z matrix of the optimized structure of CPCA. All distances are in angstroms and angles are in degrees. Note the use of dummy atoms (denoted by X) to maintain the symmetry of the molecule.

C						
X	1	1.0				
X	1	1.0	2	90.0		
X	1	1.0	2	90.0	3	180.0
X	1	1.32584738	3	90.0	2	90.0
C	5	0.74276658	1	90.0	3	0.0
C	5	0.74276658	1	90.0	4	0.0
X	1	1.0	3	90.0	2	180.0
X	1	1.58842118	3	90.0	2	90.0
X	1	1.59073039	3	90.0	2	90.0
X	9	0.91012968	1	90.0	2	0.0
X	10	0.8977025	1	90.0	2	180.0
H	11	1.24333438	9	90.0	1	90.0
H	11	1.24333438	9	90.0	1	-90.0
H	12	1.26554313	10	90.0	1	90.0
H	12	1.26554313	10	90.0	1	-90.0
C	1	1.47854355	2	32.11990444	3	90.0
H	1	1.07252971	8	31.66556562	3	-90.0
O	17	1.20813447	1	123.97618571	2	0.0
O	17	1.35723067	1	116.46811705	8	0.0
H	20	0.94996135	17	116.77710261	1	0.0

3.6 Frequency Calculations

Frequency calculations run on the optimized geometry of CPCA resulted in 30 vibrational modes. For each mode the symmetry for the mode is also represented.For each mode harmonic frequencies and force constants were obtained. Frequencies have units of cm^{-2} and force constants have units of mDyne/A and the raman scattering activites have units of A^{4}/amu.

```
                   1          2          3
                  A"         A'         A"
 Frequencies --   68.1884   271.6513   292.1192
```

```
Frc consts  --    0.0094    0.1859      0.1429
IR Inten    --    2.5843    14.3148     15.9848
Raman Activ --    0.6916    1.0926      1.0972

                    4         5            6
                   A"         A'           A'
Frequencies --   458.7538     476.0530     690.3387
Frc consts  --     0.1397     0.6188       1.2949
IR Inten    --   188.8731     0.3760       8.9924
Raman Activ --     1.7033     5.3103       2.3380

                    7         8            9
                   A"         A'           A"
Frequencies --   807.8852     861.5403     900.9353
Frc consts  --     1.9617     0.8569       0.9177
IR Inten    --    25.3939     24.8823      6.3023
Raman Activ --     2.6131     11.8063      15.7936

                   10         11           12
                   A'         A'           A"
Frequencies --   906.0032     1015.4965    1042.2540
Frc consts  --     0.6265     2.9096       1.3186
IR Inten    --     8.4709     31.0287      10.9625
Raman Activ --     2.2010     13.0064      9.9915

                   13         14           15
                   A'         A'           A"
Frequencies --  1228.2116     1232.3850    1242.2499
Frc consts  --     1.1548     1.1325       0.9984
IR Inten    --    18.1601     8.3404       10.8546
Raman Activ --     2.5885     7.4003       1.8352

                   16         17           18
                   A'         A"           A'
Frequencies --  1253.3388     1296.2870    1320.0620
Frc consts  --     1.8806     1.3494       2.4212
IR Inten    --    11.1141     2.3330       38.8703
Raman Activ --     5.4786     0.1737       23.3765
```

```
                   19         20            21
                   A"         A'            A'
Frequencies --  1342.4021     1363.0218     1570.3561
Frc consts  --     1.4614     2.2186        2.5354
IR Inten    --     0.1365     549.7485      107.5465
Raman Activ --     6.4013     4.0935        12.2468

                   22         23            24
                   A"         A'            A'
Frequencies --  1621.3750     1650.9373     1933.3590
Frc consts  --     1.6831     2.0437        19.8460
IR Inten    --     5.7256     9.8811        275.0627
Raman Activ --     7.2616     9.5286        9.0248

                   25         26            27
                   A"         A'            A'
Frequencies --  3328.7661     3334.6780     3353.0102
Frc consts  --     6.8696     6.9624        7.2222
IR Inten    --     9.6271     7.6830        11.6496
Raman Activ --    24.7889     111.6933      106.2108

                   28         29             30
                   A"         A'             A'
Frequencies --  3420.8759    3435.4710       4048.3899
Frc consts  --     7.7069    7.7578          10.3083
IR Inten    --     1.0029    5.0294          84.1097
Raman Activ --    77.7628    25.7909         62.8804
```

3.7 Visualization

All the following images were generated using Molekel running on Linux. The website for this software has been mentioned earlier.

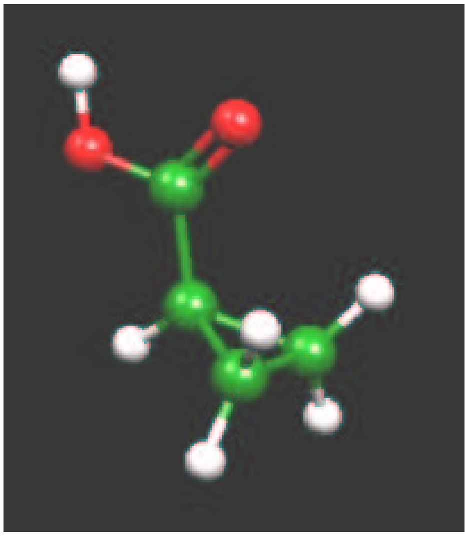

Figure 1. Optimized Geometry of CPCA

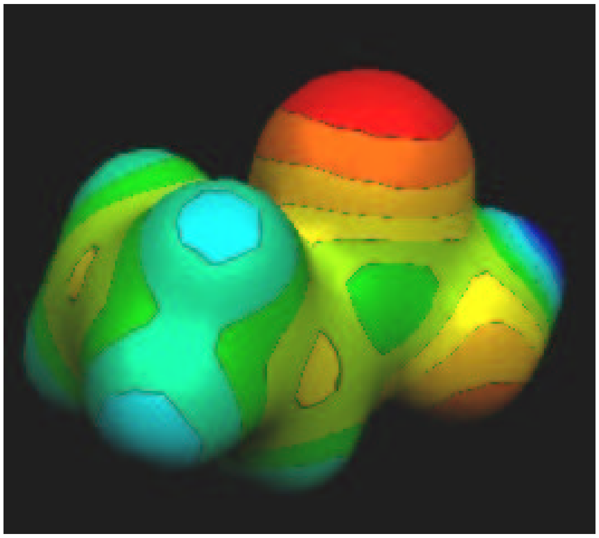

Figure 2. Electrostatic potential map of CPCA

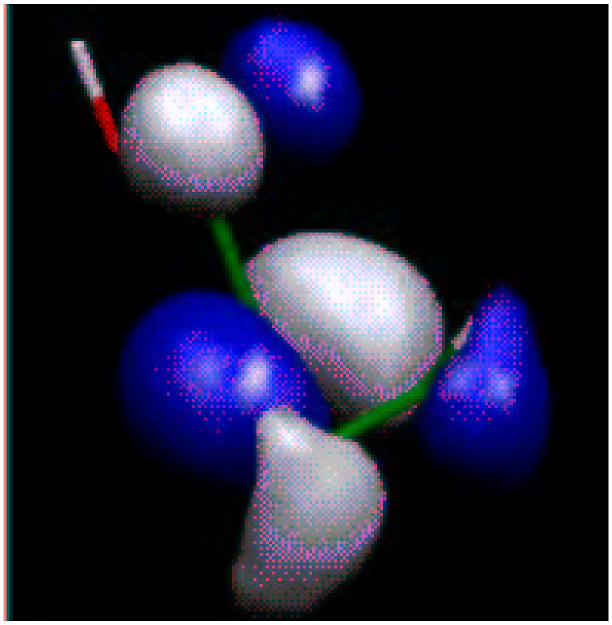

Figure 3. HOMO of CPCA

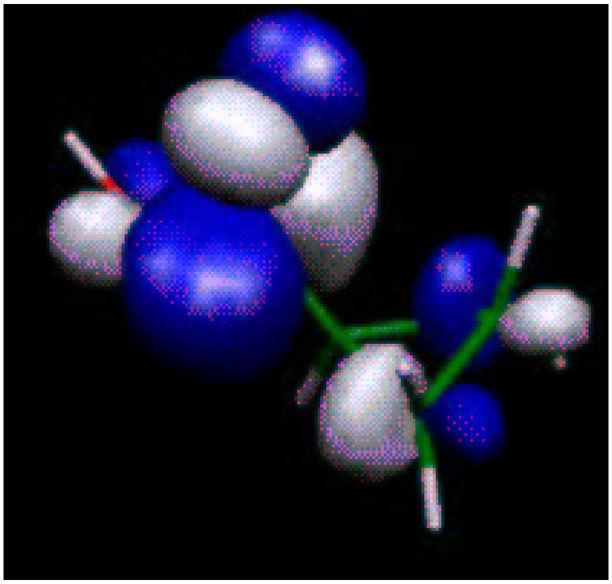

Figure 4. LUMO of CPCA

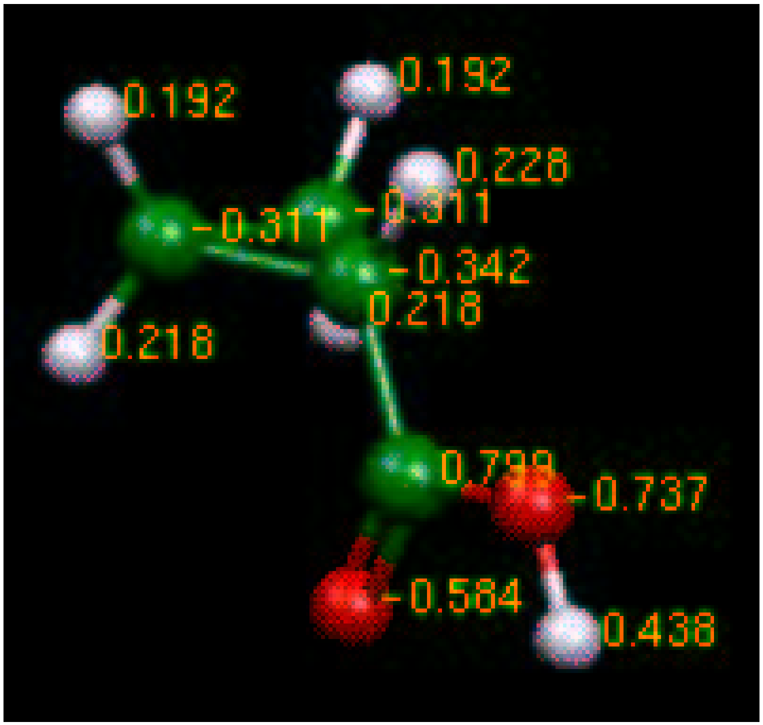

Figure 5. Charges on each atom of CPCA

References

1. Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971,** *54,* 724.
2. Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972,** *56,* 2257.
3. Hariharan, P. C.; Pople, J. A. *Mol. Phys.* **1974,** *27,* 209.
4. Gordon, M. S. *Chem. Phys. Lett.* **1980,** *76,* 163.
5. Hariharan, P. C.; Pople, J. A. *Theo. Chim. Acta.* **1973,** *28,* 213.
6. Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969,** *51,* 2657.
7. Collins, J. B.; Schleyer, P. v. R.; Brinkley, J. S.; Pople, J. A. *J. Chem. Phys.* **1976,** *64,* 5142.
8. Brinkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980,** *102,* 939.
9. Gordon, M. S.; Brinkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982,** *104,* 2797.
10. Pietro, W. J.; Frand, M. M.; Hehre, W. J. Defrees, D. J.; Pople, J. A.; Brinkley, J. S. *J. Am. Chem. Soc.* **1982,** *104,* 5039.
11. Dunning, T. H.; Hay, P. J. Modern Theoretical Chemistry. In ; Scheafer, H. F., Ed.; Plenum: New York, 1976.
12. Head Gordon, M.; Pople, J. A.; Frisch, M. J. *Chem. Phys. Lett.* **1988,** *153,* 503.
13. Frisch, M. J.; Head Gordon, M.; Pople, J. A. *Chem. Phys. Lett.* **1980,** *166,* 281.
14. Head Gordon, M.; Head Gordon, T. *Chem. Phys. Lett.* **1994,** *220,* 122.
15. Saebo, S.; Almlof, J. *Chem. Phys. Lett.* **1989,** *154,* 83.

16. Pople, J. A.; Seeger, R.; Krishnan, R. *Int. J. Quant. Chem Symp* **1977,** *11,* 149.
17. Pople, J. A.; Brinkley, J. S.; Seeger, R. *Int. J. Quant. Chem. Symp.* **1978,** *10,* 1.
18. Krishnan, R.; Schlegel, H. B.; Pople, J. A. *J. Chem. Phys.* **1980,** *72,* 4654.
19. Raghavachari, K.; Pople, J. A. *Int. J. Quant. Chem.* **1981,** *20*, 167.
20. Hohenberg, P.; Kohn, W. *Phys. Rev. B* **1964,** *136,* 864.
21. Slater, J. C. *Quantum Theory of Molecules and Solids;* volume 4 McGraw-Hill: New York, 1974.
22. Becke, A. D. *Phys. Rev. A* **1988,** *38,* 3098.
23. Frisch, M. J.; Head Gordon, M.; Pople, J. A. *Chem. Phys. Lett.* **1990,** *166,* 275.
24. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988,** *37,* 785.
25. Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989,** *157,* 2000.