Conformational Analysis of 2,6-difluorobenzoic acid

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Introduction

2,6-difluorobenzoic acid is an organic compound relating to the o-methoxybenzoic acid group. It is considered to be the major degradation of diflubenzuron, an insecticide used in forest management. The group of benzoic acids generally are used for industrial environments to manufacture perfumes, dyes, and insect repellents. Relating to its group of benzoic acid and being the degradation of diflubenzuron, 2,6-difluorobenzoic acid has been known to be used when dealing with pesticides and algae such as Euglena gracilis Z. In addition, it has become a major component in oil field applications as a chemical water tracer due to its high solubility. The geometry of 2,6-difluorobenzoic acid was optimized using quantum chemical calculations. The rotational constants and dipole moments were calculated to help further experimental study using microwave spectroscopy.

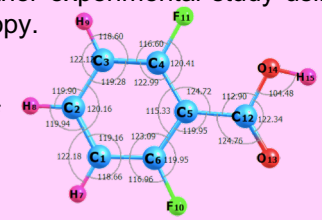


Figure 1. Calculated molecular structure of 2,6-difluorobenzoic acid

Method

Calculations were carried out with Gaussian 16 using the cluster computers from the Texas Advanced Computing Center (TACC) in order to determine the conformations of 2,6-difluorobenzoic acid. We started with potential energy scans (PES) using aug-cc-pVTZ basis set to obtain results along the dihedral angle of C_4-C_5-C_{12}-O_{14}. A scan was run at every 10 degrees for a total of 36 steps. From the potential energy scan, four equivalent forms of one most stable conformer was identified. We optimized this conformation using Density Functional Theory (DFT) and Second Order Møller–Plesset perturbation theory (MP2) with an aug-cc-pVTZ basis set to obtain the geometry of 2,6-difluorobenzoic acid.

Results

A potential energy scan was performed at the MP2/aug-cc-pVTZ level along the dihedral angle at C_4-C_5-C_{12}-O_{14}. The result is shown below in Figure 2. Four minimums were identified. Optimizations were run at the first two minimums under B3LYP/aug-cc-pVTZ and MP2/aug-cc-pVTZ but were converged to the one structure shown in Table 1.

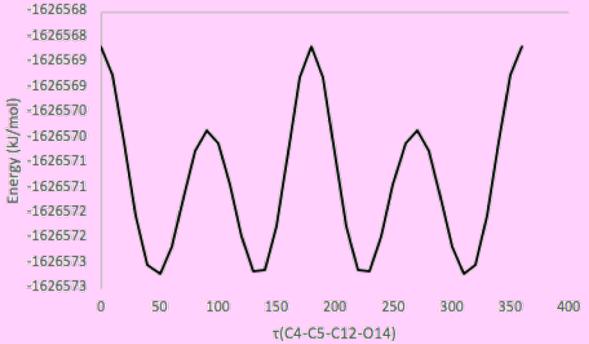


Figure 2. Potential Energy Scan along the dihedral angle C_4-C_5-C_{12}-O_{14}.

The rotational constants and dipole moments are also listed in Table 1. The calculated parameters were used to simulate the rotational spectrum to aid the future data analysis of the experimental spectrum. Based on the calculated dipole moments, the spectrum features all three types of rotational transitions.

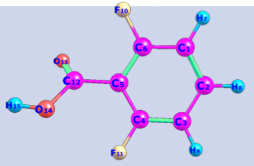
Parameters		
Structure		
Method/Basis Set	B3LYP/aug-cc-pVTZ	MP2/ aug-cc-pVTZ
A (MHz)	1529.7	1529.6
B (MHz)	1156.8	1154.8
C (MHz)	695.7	701.3
μ_a (Debye)	2.4	2.3
μ_b (Debye)	1.1	1.0
μ_c (Debye)	1.0	1.0

Table 1. Rotational constants, *A*, *B*, and *C*, and the dipole moments, μ_a, μ_b, and μ_c, calculated at the B3LYP/aug-cc-pVTZ and MP2/aug-cc-pVTZ levels.

Results cont…

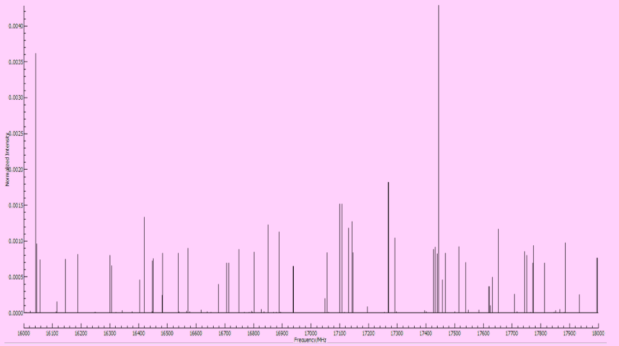


Figure 3. Simulated microwave spectrum for 2,6-difluorobenzoic acid.

Conclusion

We report the conformational analysis of 2,6-difluorobenzoic acid. Four equivalent minimums were observed in the scan, producing the same lowest energy conformer. The molecular structure of this conformer was reoptimized and the calculated rotational constants and dipole moments were used to simulate the microwave spectrum to aid the future spectroscopic search of 2,6-difluorobenzoic acid.

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