TOLU OMOTUNDE
CHE 596 HOMEWORK 2 SUMMARY

Geometry of trans-Azobenzene

Bond Lengths(pm)

	MP2 cc-pVTZ	DFT-BP86 TZVP	Expt(GE)	Expt(X-ray)	Gaussian B3LYP (HW)
N(7)-N(8)	126.8	126.7	126.0(8)	124.7	126.1
C(2)-N(7)	141.7	142.0	142.7	142.8	141.9
C(2)-C(3)	139.7	140.5	140.1	138.9	140.1
C(2)-C(1)	140.0	140.9	140.5	138.7	140.6
C(3)-H(15)	108.1	109.1	110.2(7)		108.6
C(1)-H(19)	108.0	109.0	110.2(7)		108.4

Angles, deg

	MP2 cc-pVTZ	DFT-BP86 TZVP	Expt(GE)	Expt(X-ray)	Gaussian B3LYP (HW)
C(2)-N(7)-N(8)	113.7	114.8	113.6		114.8
C(3)-C(2)-N(7)	115.1	115.3		115.6	115.3
C(1)-C(2)-N(7)	124.6	124.8		123.7	124.8
C(1)-C(2)-C(3)	120.3	119.8		120.7	119.9
C(2)-C(1)-C(6)	119.3	119.6		119.1	119.6
C(2)-C(3)-C(4)	121.1	120.2		119.6	120.2
C(2)-C(3)-H(15)	118.3	118.2			118.2
C(2)-C(1)-H(19)	119.1	118.8			118.8

Selected bond lengths and angles of the MP2/cc-pVTZ equilibrium geometry in comparison to experimental data, DFT-BP86/TZVP and Gaussian B3LYP/6-31G(d) results.

Considering this, we find the experimental and the ab initio results for the C-N and C-C distances agree within the uncertainties of the calculations and the experiment. Larger deviations are only found for the C-H (1-2 pm) and the N=N (1 pm) bond lengths. However, for the latter, the experimental result carries a large uncertainty of 0.8 pm, while C-H bond lengths are in general difficult to determine experimentally, which is reflected by the large uncertainty of the GED values. The angles are described well by the 3 methods. The largest deviations to the experimental values are about 1° for the 3 methods.

Electronic Spectra of trans-Azobenzene

The most prominent feature in the experimental absorption spectrum of trans-azobenzene is constituted by the $\pi\pi^*$ excitation into the S_2 state. The calculated results for this transition are 4.04 eV (CC2), 3.90 eV (SOPPA), 3.29 eV (DFT) and 3.4eV (B3LYP). They all give the largest oscillation strength for this excitation.