CONFORMATION SPECIFIC SPECTROSCOPY OF 4-PHENYL-1-BUTYNE, 5-PHENYL-1-PENTYNE, AND 3-BENZYL-1, 5-HEXADIYNE

TALITHA M. SELBY, ALOKE DAS, and TIMOTHY S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN 47907 U.S.A..*

4-Phenyl-1-butyne, 5-phenyl-1-pentyne, and 3-benzyl-1,5-hexadiyne were studied by a combination of methods, including resonant two photon ionization, UV-UV hole-burning spectroscopy, resonant ion-dip infrared spectroscopy, and rotational band contour studies. There are two conformations of 4-phenyl-1-butyne observed in the expansion with their $S_1 \leftarrow S_0$ origins occurring at 37617 and 37620 cm^{-1}. *Ab initio* calculations show that there are also only two low energy conformations (with the chain anti or gauche with respect to the ring). The experimental rotational band contours of the origin bands were compared to *ab initio* calculations to make conformational assignments. The gauche and anti conformations are assigned to the red and blue-shifted conformers, respectively. Three conformations of 5-phenyl-1-pentyne are observed in the expansion with their $S_1 \leftarrow S_0$ origins at 37538, 37578, and 37601 cm^{-1}. *Ab initio* calculations predict four low energy structures (two gauche and two anti). Rotational band contour analysis was used to assign the three conformations observed. The two red-shifted conformations are assigned to gauche structures. In 3-benzyl-1, 5-hexadiyne, 5 conformations are observed in the expansion with their electronic $S_1 \leftarrow S_0$ origins spread over about 100 cm^{-1}. DFT calculations predict six low energy conformations. Conformational assignments have been made by comparison of the experimental infrared spectra in the hydride stretch region to DFT frequency calculations. The electronic origin shifts of 3-benzyl-1,5-hexadiyne compare favorably to the origin shifts of 5-phenyl-1-pentyne with the exception of one conformation. This conformation is unique in that it is the only structure with both acetylenic groups in the gauche position over the ring. This gauche-gauche conformation produces extensive vibronic coupling typical of symmetric mono-substituted benzenes. The conformational isomerization energetics of 4-phenyl-1-butyne, 5-phenyl-1-pentyne, and 3-benzyl-1,5-hexadiyne will also be discussed.