3-benzyl-1,5-hexadiyne attracted our attention because it incorporates an ultraviolet chromophore attached to a side chain (1,5-hexadiyne) that can undergo structural isomerization. The cyclization of 1,5-hexadiyne is known to occur by thermal rearrangement to products such as dimethylenecyclobutene, fulvene, and benzene. The jet-cooled resonance enhanced two photon ionization spectrum of 3-benzyl-1,5-hexadiyne exhibits transitions due to 5 conformations. The $S_0$-$S_1$ origins of these conformers lie within 150 cm$^{-1}$ of the most stable conformation. UV-UV holeburning spectroscopy has been employed to obtain the $S_0$-$S_1$ vibronic spectrum of each conformation. Resonant ion-dip infrared spectroscopy was used to show each conformation has a unique ground state infrared spectrum in the CH stretch region. The acetylenic CH stretch transitions are especially sensitive to the orientation of the two acetylenic groups relative to each other, and have been very useful in assigning anti vs. gauche conformations. The anti or gauche orientation of the gamma methylene group relative to the ring also serves as a sensitive marker by shifting the electronic origins.