ymmetric ring puckering potential in thietane-1,1-dioxide compared with experiment and analysis of theoretical vibrational spectra. Forner, Wolfgang; Badawi, Hassan M.. Chemistry Department, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia. International Journal of Quantum Chemistry (2006), Volume Date 2007, 107(2), 469-479.

Abstract

We studied the ring puckering potential in thietane-1,1-dioxide with different methods, using a suitable basis set, 6-311+G**. We obtained a barrier to ring puckering of 153 cal/mol with the DFT/B3LYP (Becke3 exchange-Lee, Yang, Parr correlation functional) method, .apprx.60% too small compared with expt. However, using MP2, MP3, and MP4 we obtained values around 200% too large. The MP series turned out to converge far too slowly to the exptl. barrier value, showing no sign of convergence even at MP4, while higher orders are out of our reach for such a system. Obviously, of all methods used, DFT worked best despite some shortcomings. The barrier corresponds to 77 K; thus, there should be rapid interconversion over the barrier at room temp., a phenomenon actually obsd. at room temp., the measured barrier corresponding to 201 K. Thus, we decided to use the DFT/6-311+G** calcns. to predict reasonable vibrational spectra and assignments of the lines found. The ring puckering mode is found at 80 cm-1 in DFT in good agreement with the exptl. value of 78.3 cm-1 for this vibration.