

## Theoretical vibrational spectra of organic ring compounds compared to experiment.

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### Abstract

We have studied vibrational IR and Raman spectra of several org. ring compds. These include first cyclobutanecarboxaldehyde (CBA) and cyclohexanecarboxaldehyde (CHA) using d. functional theory (DFT) together with a Becke-3 exchange and Lee-Yang-Parr correlation (B3LYP) functional. DFT in these systems gives a stable and low-energy gauche-axial (g-ax) conformer for both of the mols. together with the exptl. found equatorial conformations. However, on the basis of comparison of the theor. vibrational spectra of the conformational mixt. at 300 K with exptl. spectra, the presence of the g-ax conformer could be ruled out because it would yield extra lines not present in the corresponding exptl. spectra. Thus, we concluded that DFT yields properties related to energy derivs. such as min. geometries and vibrational spectra in fair agreement with expt., while total energy differences are not trustworthy when they are small, esp. if small linear dependencies in the at. basis sets applied appear. However, in that case we found that Moller-Plesset perturbation theory of second order (MP2) applied to CBA has the same problems and even does not predict the abs. min. on the potential hypersurface correctly. Therefore, we applied DFT also to biphenyle (BP) and terphenyle (TP). Again, in BP and TP DFT turned out to yield reliable structures that as far as the important torsional angle between the rings is concerned are even better than MP2. Also, the vibrational spectra are in fair agreement with exptl. ones. In BP RHF, DFT and exptl. IR spectra all show two intense absorptions around 700 cm<sup>-1</sup>, while MP2 gives only one intense absorption band in this region. DFT also reproduces the position of these two lines well.