

Conformer determination of stabilized triphenyl phosphonium acyl ylides by infrared spectroscopy

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Stretching frequencies of acyl groups of stabilized triphenyl phosphonium ylides with ester, keto or cyano groups depend in part on the orientations of the acyl groups, syn or anti, with respect to phosphorus. Frequencies predicted by ab initio HF methods are higher than observed, and for diesters and diketones are higher for anti than syn acyl groups. For diester and diketo ylides and their cyano derivatives a Scale Factor, SF, of 0.866, fits much of the data with HF/6-31G(d) calculations, although it is lower than the literature value. The literature SF values for DFT methods, e.g., BLYP/6-31G(d) and B3LYP/6-31G(d), are closer to unity, and agreement with experiment is reasonable, except that for mixed anti isopropoxy or t-butyloxy and syn methoxy or ethoxy diester ylides predicted stretching frequencies of the syn acyl groups by BLYP are too low, and fits are worse than with HF/6-31G(d), but B3LYP gives satisfactory results. The combination of ab initio methods and determination o