# Comparison of conformations of diesters of stabilized phosphonium ylides in solution and in the crystal

Castañeda, Fernando

Silva, Paul

Garland, M. Teresa

Shirazi, Ata

Bunton, Clifford A.

Computed bond lengths and angles of methyl ethyl and dimethyl triphenyl phosphonium ylidic diesters, 1b, c, respectively, are similar to those in the crystal, as for the diethyl ester, 1a, where both acyl oxygens are anti to phosphorus. The 1H and 13C NMR spectra of the methyl ethyl diester, 1b, where one acyl oxygen is syn and the other anti to phosphorus, are as expected in terms of the conformation in the crystal, but the dimethyl ester, 1c, in the crystal is an equimolar mixture of conformers. For a given ylidic diester the different conformers have similar energies from B3LYP//6-31G(d) computations, interconversions of conformers should not be slow at ambient temperatures and 1H and 13C NMR signals in solution are sharp. Estimation of Natural Atomic Charges indicates significant cationoid character on phosphorus and the acyl carbons, and anionoid character on the ylidic carbon and the ester oxygens depending on orientations towards phosphorus.