CONFORMATIONS OF TRIMETHYL PHOSPHITE: A MATRIX ISOLATION INFRARED AND AB INITIO STUDY

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Hyperconjugative interactions have received considerable attention because of its importance in determining structure and reactivity in organic compounds. In all these molecules, our studies, as many others in the literature, indicated that the $O-P-O$ and $O-C-O$ segments played a crucial role in conformational preferences. In the case of the organic phosphates, in addition to the $O-P-O$ segments, the $P=O$ group was also found to influence the structures. To address this issue further, it was thought interesting to study the conformations of trimethylphosphite (TMPhite), which lacks a $P=O$ group. A comparison of the conformations of trimethylphosphate (TMP) and TMPhite was expected to highlight the role of the $P=O$ group in the conformational preference of organic phosphates, which is the motivation for the present work. The conformations of TMPhite were studied using matrix isolation infrared spectroscopy. TMPhite was trapped in a nitrogen matrix using an effusive source maintained at 298 K and 410 K and also a supersonic source. These experiments were designed to enable us to assign the infrared features of the higher energy conformer(s). As a result of these experiments, infrared spectra of the conformations of TMPhite were obtained. The experimental studies were supported by ab initio computations performed at the $B3LYP/6-31++G**$ level. Computations indicated four minima corresponding to conformers with the following symmetries: C_1, C_s, C_{1a} and C_3, given in order of increasing energy. This conformational picture was clearly different from that of TMP, in which the C_3 was the lowest energy structure, thereby clearly indicating the role of the $P=O$ group in structural preferences in these systems. We also performed a photochemical insertion of oxygen in TMPhite to produce TMP in the matrix, in an effort to correlate the conformers of the two molecules. These experiments also gave rise to interesting side reactions, where in addition to TMP, we also observed the products where oxygen appeared to be inserted into the $P-O-Me$ moiety. The conformational landscape of the two molecules has also been rationalized using Natural Bond Orbital (NBO) analysis.