Molecular Structure and Conformational Preferences of Trimethyl Phosphorotrithioite, $P(SMe)_3$, Evaluated by Gas-Phase Electron Diffraction and Quantum Chemical Calculations

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Abstract — Free $P(SMe)_3$ molecule was studied by gas electron diffraction (GED) and by B3PW91/6-311+G* (DFT) and MP2/6-31+G* calculations. Each conformer is characterized by three dihedral angles τ(CSP*lp*), where *lp* denotes the direction of the lone electron lone pair on the P atom. DFT calculations indicate that the most stable conformer is an *anti*,*gauche*+,*gauche*– (*ag*+*g*–) conformer of C_s symmetry; the next are the *ag*+*g*+ (ΔE = 2.5 kJ mol^{-1}), *g*+*g*+*g*+ (ΔE = 5.2 kJ mol^{-1}), and *aa*+*g*+ (ΔE = 12.5 kJ mol^{-1}) conformers. The MP2 calculations give the similar order, with the relative energies of 0.3, 4.3, and 10.6 kJ mol^{-1}, respectively. The experimental GED data agree well with the presence of only two conformers: χ(*ag*+*g*+) = 80(20)% and χ(*ag*+*g*–) = 20(10)%.