Structures, Bonding, and Energetics of Potential Triatomic Circumstellar Molecules Containing Group 15 and Group 16 Elements

Walter E. Turner II

The recent discovery of PN in the oxygen-rich shell of the supergiant star VY Canis Majoris points to the formation of several triatomic molecules involving oxygen, nitrogen, and phosphorus; these are also intriguing targets for main-group synthetic inorganic chemistry. In this research, high-level *ab initio* electronic structure computations were conducted on the potential circumstellar molecule OPN and several of its heavier group 15 and 16 congeners (SPN, SePN, TePN, OPP, OPAs, and OPSb). For each molecule, four isomers were examined. Optimized geometries were obtained with coupled cluster theory [CCSD(T)] using large Dunning basis sets [aug-cc-pVQZ, aug-cc-pV(Q+d)Z, and aug-cc-pVQZ-PP], and relative energies were determined at the complete basis set limit of CCSDT(Q) from focal point analyses. The linear phosphorus-centered molecules were consistently the lowest in energy of the group 15 congeners by at least 6 kcal mol^{-1}, resulting from double-triple and single-double bond resonances within the molecule. The linear nitrogen-centered molecules were consistently the lowest in energy of the group 16 congeners by at least 5 kcal mol^{-1}, due to the electronegative central nitrogen atom encouraging electron delocalization throughout the molecule. For OPN, OPP, and SPN, anharmonic vibrational frequencies and vibrationally-corrected rotational constants are predicted; good agreement with available experimental data is observed.