Infrared Spectra of the 2,3-Dihydropyrrol-2-yl and 2,3-Dihydropyrrol-3-yl Radicals Isolated in Solid *para*-Hydrogen

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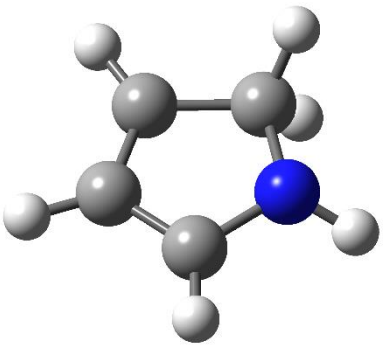
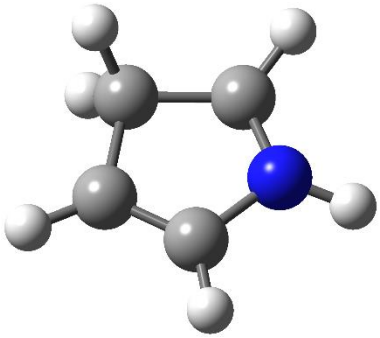
The reaction of hydrogen atoms (H) with pyrrole (C_4H_5N) in solid *para*-hydrogen (*p*-H_2) matrices at 3.2 K has been studied using infrared spectroscopy. The production of H atoms for reaction with C_4H_5N was essentially a three step process. First, mixtures of C_4H_5N and Cl_2 were co-deposited in *p*-H_2 at 3.2 K for several hours, then the matrix was irradiated with ultraviolet light at 365 nm to produce Cl atoms from the Cl_2, and finally the matrix was irradiated with infrared light to induce the reaction of the Cl atoms with *p*-H_2 to produce HCl and H atoms. Upon infrared irradiation, a series of new lines appeared in the infrared spectrum, resulting from the products of the H + C_4H_5N reaction. To determine the grouping of lines to distinct chemical species, secondary photolysis was performed using 533-nm and 455-nm light-emitting diodes. Based on the secondary photolysis, it was determined that the majority of the new lines belong to two distinct chemical species, designated as set A (3491.0, 3111.7, 2754.4, 2693.3, 1412.7, 1260.4, 1041.8, 963.2, 922.0, 674.2 cm^{-1}) and set B (3468.3, 3124.9, 3109.9, 3099.7, 2784.9, 2732.4, 1470.6, 1449.5, 1366.3, 1266.2, 1151.1, 1117.2, 1098.0, 1042.8, 960.6, 949.5, 924.0, 860.8, 574.2 cm^{-1}). The most likely reactions to occur under the low temperature conditions in solid *p*-H_2 are the addition of the H atom to the nitrogen atom or the two carbon atoms of C_4H_5N to produce the corresponding hydrogen atom addition radicals (H-C_4H_5N). Quantum-chemical calculations were performed at the B3PW91/6-311++G(2d,2p) level for the three possible H-C_4H_5N radicals in order to determine the relative energetics and the predicted vibrational spectra for each radical. The addition of the H atom to carbons 2 and 3 is predicted to be exothermic by 112.1 and 76.1 kJ/mol, respectively, while the addition of the H atom to the nitrogen is predicted to be endothermic by 67.8 kJ/mol. When the lines in set A and B are compared to the scaled harmonic and anharmonic vibrational spectra for all three possible radicals, the best agreement for set A is with the radical produced by the addition to carbon 3 (2,3-dihydropyrrol-2-yl radical) and the best agreement for set B is with the radical produced by addition to carbon 2 (2,3-dihydropyrrol-3-yl radical). In addition to the assignments of the 2,3-dihydropyrrol-2-yl and 2,3-dihydropyrrol-3-yl radicals, a series of lines that appear upon 455 nm photolysis (3114.2/3113.4, 3092.7, 3034.8/3034.3, 2925.9/2925.0, 2906.7/2905.8, 1589.6, 1489.8, 1377.6, 1347.9, 1096.8, 990.1/989.1, 964.0/962.7, 917.0, 884.3, 845.8, 822.0, 686.4, and 536.3/533.9 cm^{-1}) have been assigned to 1,3-pyrrolenine.



2,3-dihydropyrrol-3-yl radical



2,3-dihydropyrrol-2-yl radical