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Synthesis, crystal structures and quantum chemical calculations of novel phosphonium salt-1, 5-diphospha-3-phosphonia-tricyclo pentane cations**Mutasem Z Bani-Fwaz and Ahmed E Fazary**
King Khalid University, KSA

This work deals with reactions between the kinetically stable 2-tert-butyl-1 λ^3 -phospha-alkyne, tBu C=P, and various halodiorganylphosphines (X=Cl, Br). The isolated ionic salts with the 2, 4-di-tert-butyl-3, 3-diorganyl-1 λ^3 , 5 λ^3 -diphospha-3-phosphonia-tricyclo [2.1.0.02,5]-pentane cations, [R²C²tBu²P³] (R=ethyl, isopropyl, methyl, phenyl), were characterized by spectroscopic methods; additionally, the results of X-ray structure analyses were confirmed by quantum chemical calculations which were performed on the hydrogen substituted phosphonium and phosphonium cations. As for the phosphonium cation ([H₂P(CH)₂P²]) generated from our work the conventional trigonal bipyramidal framework of point group C_{2v} represents the absolute minimum on the potential energy surface. To our surprise this situation is followed by a second one which has to be attributed to the so-called housene structure of point group C₁ showing a somewhat higher energy value +77.9 kJ/mol. Quite a reverse situation is encountered for the phosphonium cation [P(CH)₂P₂]. Here the pseudo square-based pyramidal nido structure of point group C_{2v} known from Russell's tetrachloroaluminate(III) compound is found to be the only minimum on the potential energy surface. A phosphonium cation with a trigonal bipyramidal framework of point group C_{2v} is higher in energy only by 35.7 kJ/mol but due to one imaginary frequency it has to be considered the structure of a transition state. The opened housene structure corresponds neither to a minimum nor to a saddle point on the potential energy surface. In the pseudo square-based pyramidal nido structure (point group C_{2v}) of the phosphonium cation [P(CH)₂P₂] the s-orbital and all p-orbitals of the apical four-coordinate phosphorus atom are used to form two P-C and two P-P bonds. Further addition of two hydrogen atoms to entail the phosphonium cation [H₂P(CH)₂P₂] of point group symmetry C₂ not only increases the coordination number of the apical phosphorus atom to six but also requires two electrons and two orbitals for P-H bonding.

banifawaz@yahoo.com