

含S-P-N键的磷烯正离子及其相关物的结构和性质的从头计算

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摘要 本文对5-甲硫基-3-N-苯基-2,3-2(H)-1,3,4,2-噻二唑磷茂啉的磷烯正离子等三个相关分子的平衡几何构型进行了从头算解析能量梯度方法的全优化计算. 优化结果表明, 二配位磷烯正离子与相应的三配位磷母体分子的结构有本质的差异. 形成二配位磷烯正离子后, 磷所在的五员环形成共轭体系而使原来的单键键长变短, 原来的双键键长变长, 且使原来不共面的五员环共面. 在优化的平衡几何处进行单点CI计算的结果表明, 基态分子中磷原子上的正电荷的相对多少次序与实验测得的摩尔电导率及 ^{31}P NMR谱的化学位移的相对大小次序完全一致.

关键词 [结构分析](#) [化学键](#) [从头计算法](#) [净电荷](#) [平衡状态](#) [磷烯正离子](#)

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Ab Initio calculations of molecular geometries and properties of phosphonium cation featuring with S-P-N bond and the related others

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Abstract The equilibrium geometries of 5-Methylthio-3-N-phenyl- 2,3-2(H)-1,3,4,2-Thiadiazaphosphonium Cation and other two related organophosphorus molecules have been optimized at the level of ab initio molecular orbital calculation with STO-3G basis set by use of the analytical energy-gradient technique. The optimized geometries show that the chemical bonds in the phosphonium cations are different from those in the corresponding three-coordinated phosphorus systems. From the three-coordinated phosphorus to the phosphonium cation, because of the formation of the new conjugated system containing the phosphorus atom, the length of the single bonds become shorter and the length of the double bond become longer. The numerical results obtained from the ab initio CI calculations at the equilibrium geometries show that the relative values for the positive charges of the phosphorus atoms are in good agreement with the relative values for the chemical shift of ^{31}P NMR and for the molar conductivity .

Key words [STRUCTURAL ANALYSIS](#) [CHEMICAL BONDS](#) [AB INITIO CALCULATION](#) [NET CHARGE](#) [EQUILIBRIUM STATE](#)

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