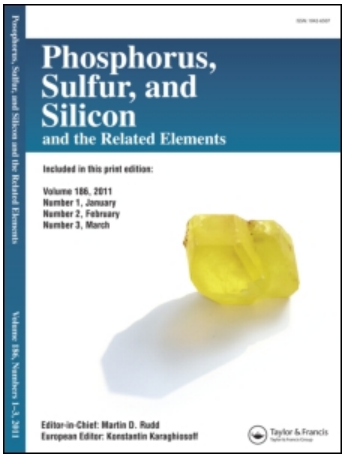

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Heidi Lange; Risto S. Laitinen

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AN *AB INITIO* MO STUDY OF PHOSPHORUS SELENIDE SULFIDES $P_4Se_xS_{3-x}$, $P_4Se_xS_{4-x}$, AND β-$P_4Se_xS_{5-x}$

HEIDI LANGE AND RISTO S. LAITINEN
Dept. of Chemistry, University of Oulu,
Linnanmaa, 90570 Oulu, Finland

The structures and stabilities of different phosphorus selenide sulfides are discussed with help of *ab initio* molecular orbital calculations. All isomers in the series $P_4Se_xS_{3-x}$, $P_4Se_xS_{4-x}$, and β-$P_4Se_xS_{5-x}$ are studied.

Keywords: phosphorus selenide sulfides, *ab initio* mo calculations

INTRODUCTION

Whereas phosphorus sulfides and selenides have seen extensive research activity,[1] the structrural information of analogous mixed phosphorus selenide sulfides is much sparser. Nuclear magnetic resonance spectroscopy has proven a useful tool in studying the structures of phosphorus chalcogenides [2] as well as molecular transformations of various phosphorus sulfides.[3] The experimental information is augmented by theoretical calculations at different levels of theory.[4,5] The present work is carried out in order to establish the correlation between the geometries and stabilities of molecules with

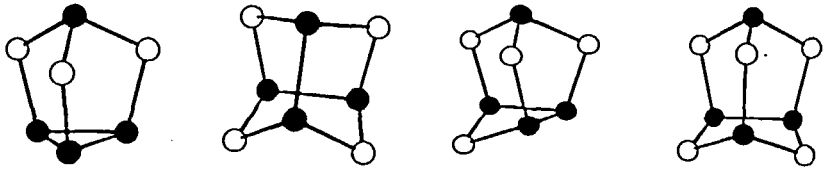
different chalcogen proportions. This study comprises all members in the series $P_4Se_xS_{3-x}$, α-$P_4Se_xS_{4-x}$ and β-$P_4Se_xS_{4-x}$, and β-$P_4Se_xS_{5-x}$. Theoretical calculations may be utilized in the preparation of novel phosphorus and chalcogen compounds.

CALCULATIONS

All MO calculations were carried out with GAUSSIAN 94 [6] involving MIDI-4* basis sets [7] augmented with *d*-polarization functions. The gradient techniques were employed in the geometry optimization of all molecules. A second order Møller-Plesset correction for electron correlation was performed using the optimized geometries.

DISCUSSION

The general conformation of each member within the four phosphorus selenide sulfide series is fairly similar and is shown in Figure 1. The calculated bond parameters are in agreement with the experimental values where available, and indicate that all phosphorus-chalcogen framework bonds are single bonds, as expected due to the known crystal structures of several phosphorus sulfides.[1] While there is no experimental structural information for mixed phosphorus chalcogenides, their calculated bond parameters are reasonable when compared to those of corresponding phosphorus sulfides and selenides.



P_4E_3 α-P_4E_4 β-P_4E_4 β-P_4E_5

FIGURE 1 General conformations of P_4E_x series.

The bond parameters also agree with those obtained by using MD/DF approach.[4] Our calculations, however, predict a decreasing order of stability as a function of selenium content within each series in contrast to the MD/DF study of Jones and Seifert.[4] This is consistent

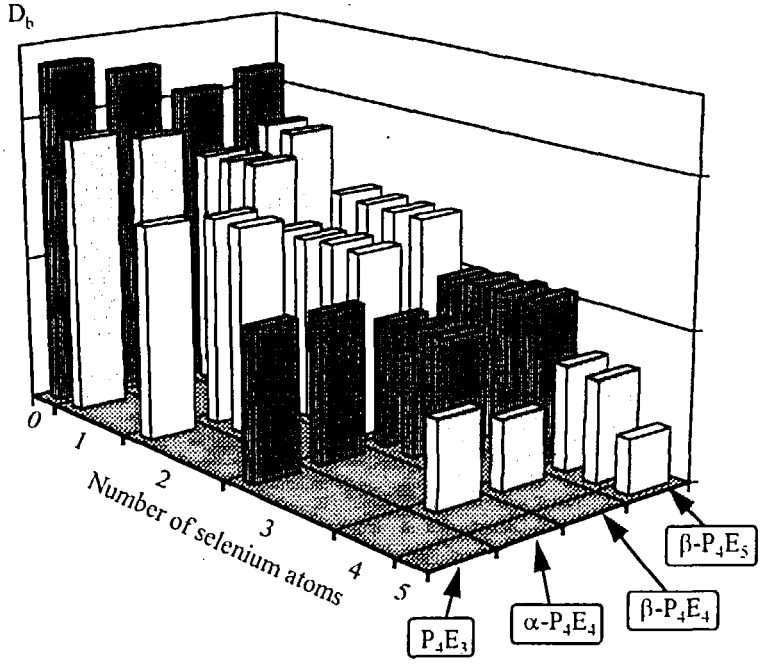


FIGURE 2 The average one-atom contribution to the total binding energy (D_b) for each isomer is obtained by subtracting the energy of free atoms from the total energy of molecule, and dividing the result by the number of atoms.

with the fact that the phosphorus-sulfur bond is stronger than the phosphorus-selenium bond.[8]

In Figure 2 the average one-atom contributions to the total binding energies are shown for the $P_4Se_xS_{n-x}$ isomers (n=3-5, x=0-n). The β-form of P_4E_4-series (C_s) is expectedly less stable than the more symmetrical α-P_4E_4 (D_{2d}) or β-P_4E_5 (C_{2v}).

Acknowledgments
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