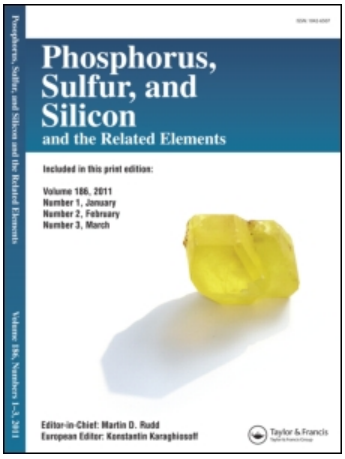

Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Suontamo, Reijo J. , Siivari, Jari , Laitinen, Risto S. and Chivers, Tristram(1994) 'Six-Membered Selenium-Sulfur Nitrides $Se_xS_{4-x}N_2$ (x = 0-4)', Phosphorus, Sulfur, and Silicon and the Related Elements, 93: 1, 245 — 248
To link to this Article: DOI: 10.1080/10426509408021826
URL: http://dx.doi.org/10.1080/10426509408021826

Phosphorus, Sulfur, and Silicon, 1994, Vol. 93–94, pp. 245–248
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SIX-MEMBERED SELENIUM-SULFUR NITRIDES $Se_xS_{4-x}N_2$ (x = 0-4)

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Abstract *Ab initio* MO calculations have established the structural and stability relationships of different members in the series 1,3-$Se_xS_{4-x}N_2$ (x = 0-4). Each molecule was found to lie in a half-chair conformation like that of 1,3-S_4N_2. The bond parameters agree well with experimental data where available. The bond lengths in the NEEEN fragment aproach those of the single bonds. The bonds in the NEN fragment show marked double bond character. The stabilities of the molecules decease expectedly with increasing selenium content as judged by the total binding energy at the MP2 level of theory. Within a given chemical composition, isomers containing a N=Se=N unit lie higher in energy than those containing a N=S=N unit. These results may explain why selenium-rich $Se_xS_{4-x}N_2$ molecules have not been isolated.

INTRODUCTION

The existence of selenium-containing analogues of S_4N_2 has been under debate. Recently, Dehnicke *et al* [1] have reported the preparation of Se_4N_2 by the reaction of dichlorodiselane with trimethylsilylazide in dichloromethane. Se_4N_2 was obtained as black powder that was said to be stable up to 80 °C. The reported stability of Se_4N_2, however, was incompatible with the earlier observation that the reaction of dichlorodiselane with trimethylsilyl azide in dichloromethane produces an explosive blue-black Se-N compound.[2] Indeed, the reinvestigation of this reaction showed the product to be violently unstable $Se_3N_2Cl_2$.[3,4]

The present study is a part of our interest in the mixed six-membered chalcogen nitrides $Se_xS_{4-x}N_2$.[5,6] *Ab initio* MO calculations on all members of the heterocyclic series $Se_xS_{4-x}N_2$ (x = 0-4) were carried out in order to establish the structural and stability relationships as a function of the selenium content in the molecule.

COMPUTATIONAL DETAILS

All MO calculations were carried out with Gaussian 92 [7] involving MIDI-4* basis sets [8] augmented by *d*-polarization functions. The gradient techniques were employed in the geometry optimization of all twelve possible isomers. A second-order Møller-Plesset correction for electron correlation [9-11] was performed using the optimized geometries. The fundamental vibrations were calculated for the optimized geometries at the HF level of theory to establish the nature of the stationary points.

RESULTS AND DISCUSSION

The MIDI-4* optimized bond parameters of all twelve possible $Se_xS_{4-x}N_2$ isomers are shown in Fig. 1. All molecules are remarkably similar and exhibit an optimum geometry with an approximate half-chair conformation that is well established experimentally for S_4N_2.[12-14] The calculated bond parameters of S_4N_2 are in good agreement with the experimental data. While there is no experimental information for other $Se_xS_{4-x}N_2$ species, their calculated bond parameters are reasonable when compared to those of S_4N_2. Whereas the NEN (E = S, Se) unit clearly shows double bond character, the bonds in the NEEEN fragments approach single bonds. The calculated HF/MIDI-4* fundamental vibrations indicate that all molecules lie in the true local energy minima.

The electronic structures of the the bonds in the NEEEN units are rather insensitive to the nature of the chalcogen atoms in the fragment. The energies of the orbitals describing the bonding in the NEN unit depend, however, on the nature of the chalcogen atom between the two nitrogen atoms. The molecular orbitals describing the bonding in the NSN unit lie systematically somewhat lower in energy than those of a NSeN unit.

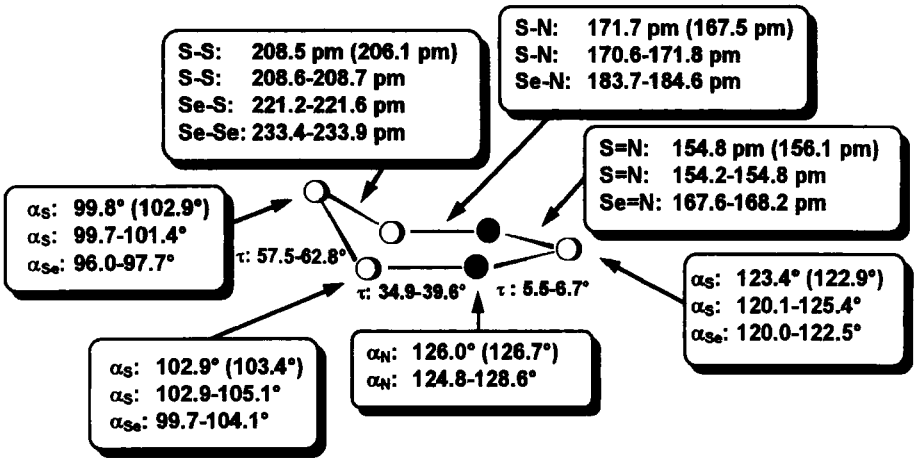

FIGURE 1. HF/MIDI-4* optimized bond parameters of $Se_xS_{4-x}S_2$ (x = 0-4). The values in parentheses are from the low-temperature crystal structure of S_4N_2.[13]

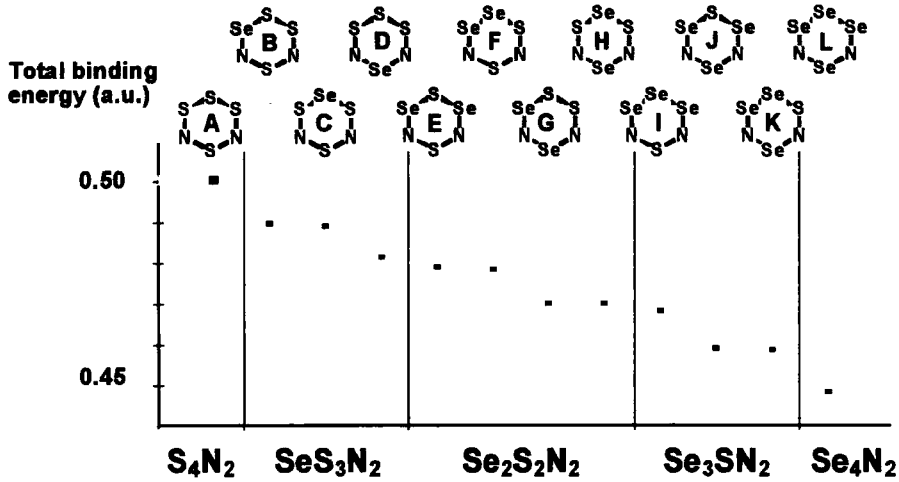

FIGURE 2. Total MP2/MIDI-4* binding energies of $Se_xS_{4-x}N_2$ (x = 0-4) (1 a.u. = 2625 kJ mol^{-1}

All molecules are stable relative to free atoms. The total binding energy diminishes as the selenium content of the molecule increases (see Fig. 2). Within a given composition isomers containing a NSeN unit show less binding than those containing a NSN unit. It can be seen from Fig. 2 that the NSeN unit is *ca.* 25 kJ mol^{-1} less stable than the NSN unit.

The selenium atoms are therefore preferably located in the NEEEN unit (E = S, Se). The relative energies of the isomers seem to be virtually independent on the distribution sulfur and selenium atoms within this fragment. The decrease of the total binding energy with increasing selenium content and the poorer stability of the NSeN fragment with respect to the NSN fragment may explain why selenium-rich $Se_xS_{4-x}N_2$ have not been isolated.

ACKNOWLEDGMENTS

The financial support from the Academy of Finland and Neste Oy Foundation is gratefully acknowledged.

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