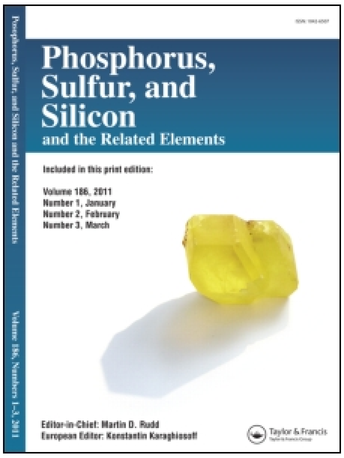

Phosphorus, Sulfur, and Silicon and the Related Elements

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 Glass, Richard S. , Pollard, John R. , Schroeder, T. Benjamin , Lichtenberger, Dennis L. , Block, Eric , Deorazio, Russell , Guo, Chuangxing and Thiruvazhi, Mohan(1997) 'Spectroscopic, Theoretical, and Electrochemical Studies of 1,2-Dithiins', Phosphorus, Sulfur, and Silicon and the Related Elements, 120: 1, 439 — 440

To link to this Article: DOI: 10.1080/10426509708545587

URL: http://dx.doi.org/10.1080/10426509708545587

Phosphorus, Sulfur, and Silicon, 1997, Vol. 120 & 121, pp. 439–440
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Spectroscopic, Theoretical, and Electrochemical Studies of 1,2-Dithiins

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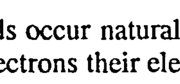
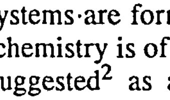
The lowest oxidation potentials for 1,2-dithiins are in the range of 0.67-0.96 V in acetonitrile and 0.81-1.04 V in dichloromethane. These oxidation potentials are less anodic than expected based on the ionization potentials of 1,2-dithiin determined by photoelectron spectroscopy. Theoretical calculations suggest that the reason for this difference is a change in optimized geometry between 1,2-dithiin and its oxidized species.

INTRODUCTION

1,2-Dithiins, **1**, have attracted considerable interest because of their novel heterocyclic system and because derivatives such as thiarubrine B (**1a**) and A (**1b**) and related compounds occur naturally in plants.[1] Since these systems are formally antiaromatic with 8π electrons their electronic structure and redox chemistry is of interest. Furthermore, oxidation of these compounds has also been suggested[2] as a basis for their light-dependent-biological activity.



1a, R = CH_2=CHC≡C-, R' = MeC≡C-C≡C-
b, R = CH_2=CHC≡C-C≡C-, R' = MeC≡C-
c, R = R' = Ph
d, R = R' = CH_2OH
e, R = R' = H



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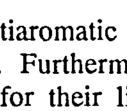

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RESULTS

Electrochemistry

The electrochemistry of **1b-e** was studied using the technique of cyclic voltammetry in both CH_3CN and CH_2Cl_2 at a scan rate of 100 mV/s versus an Ag/0.1 M $AgNO_3$ in CH_3CN reference electrode. There is a reversible oxidation at 0.67 - 0.745 V in CH_3CN and 0.81-0.85 V in CH_2Cl_2 followed by an irreversible oxidation at higher potential (1.03-1.40 V) except for **1b** which shows only irreversible oxidations at 0.96 and 1.26 V in CH_3CN and 1.04 and 1.36 V in CH_2Cl_2. For comparison purposes the oxidation potential of **2** was measured under these conditions and found to be 1.13 and 1.04 V in CH_2Cl_2 and CH_3CN, respectively.

Photoelectron Spectroscopy

The gas phase HeI spectrum of **1e** shows a distinct first ionization peak at 8.16 eV (FWHM=0.45 eV) that is well separated from the second ionization peak at 9.88 eV (FWHM = 0.59 eV), a third peak at 11.59 eV (FWHM = 0.61 eV), and the deeper valence ionizations (> 12 eV) of the molecule. The relative intensities of the first three peaks are 1:2:1. Comparison with the relative intensities of the ionizations in the HeII spectrum indicates that there are mixtures of sulfur and carbon character in the first several ionizations.

Theoretical Calculations

Geometry optimized *ab initio* calculations on **1e** show that it preferentially adopts a non-planar, twisted geometry ($<$C-S-S-C *ca.* 50°). The calculated bond lengths, bond angles and torsional angles agree very well with the geometry determined by microwave spectroscopic analysis[3] and those calculations reported previously.[4] Calculations at the UMP2/6-31G* level, as well as minimal basis-set HF and semi-empirical calculations on the cation radical predict a planar lowest energy geometry as was found previously[5] for the dication.

DISCUSSION

The lowest ionization potential for diphenyl disulfide is 8.3 eV[6] which is only slightly higher than that of **1e**, but its electrochemical oxidation is irreversible and occurs at a much higher potential (1.34 V[7]) than that of **1e**. Furthermore, the anodic peak potential for **3** of approximately 0.65 V[8] is comparable to that of **1e** but its lowest ionization potential of 7.14 eV[9] is 1 eV lower than that for **1e**. Consequently it appears that the oxidation potential of **1e** is anomalously low based on its ionization potential. Theoretical calculations suggest that this effect is primarily due to a conformational difference between **1e** and its cation radical and dication. The time scale of the electrochemical experiment allows for a geometry change of **1e** on oxidation but the much shorter time scale of the photoelectron spectroscopic measurement does not.

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