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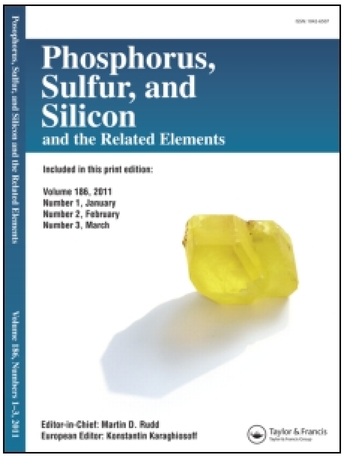

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Experimental and Theoretical Investigations of 1,4,5,7 Dithiadiazepines

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EXPERIMENTAL AND THEORETICAL INVESTIGATIONS OF 1,4,5,7 DITHIADIAZEPINES.

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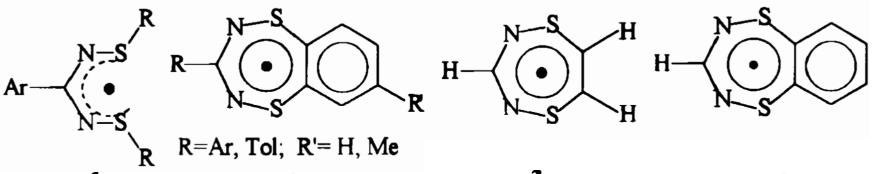
Abstract. A 1,4,5,7-dithiadiazepinyl radical has been prepared and characterized by ESR. Properties of this novel family of 9 π-electron systems are discussed on the basis of DFT calculations.

INTRODUCTION.

There is current interest in heterocyclic radicals based on carbon-nitrogen-chalcogen frameworks as potential building blocks for conducting materials. Several families of 7 π-electron heterocyclic radicals have been characterized during the last decade. Extensive studies have been published for 1,2,3,5 dithiadiazolyl radicals.[1]

The reaction of trisilylated benzamidines $ArCN_2(SiMe_3)_3$ with benzene chalcogenyl chlorides in a 1:3 molar ratio produces diazenes of the type trans-RENC(Ar)N=NC(Ar)NER (E=S, Se). The resonance-stabilized radicals $ArC(NEPh)_2{}^{\bullet}$, 1, have been identified as intermediates in this process by ESR spectroscopy,[2] but they cannot be isolated. Such radicals can be stabilized as seven-membered delocalized rings. The 1,4,5,7-dithiadiazepinyl radicals, 2, constitute a new family of 9 π-electron systems (See Scheme 1).



1 2 3 4

SCHEME 1

RESULTS

Experimental

The synthesis involves the cyclondensation of a persilylated benzamidime with a 1,2-benzene-bis(sulfenyl chloride). The resulting 4-trimethylsilyl-1,4,5,7 dithiadiazepine can be oxidized to the radical by phenylselenenyl-chloride. An alternative approach consists of the oxidation to the cationic cycle by SO_2Cl_2 followed by reduction with Ph_3Sb.

For R =H and R'= Me the ESR spectrum of 2 shows a five line pattern, which is attributed to spin delocalization over the nitrogen atoms, with g = 2.0070 and $a_{average}$ = 0.49 mT (cf. g = 2.0071 and a = 0.575 mT for 1 with Ar = R = Ph). The slight asymmetry of the spectrum reflects the molecular symmetry.

Density Functional Theory (DFT) Calculations.

The properties of 1,4,5,7-dithiadiazepinyl radicals have been modeled with DFT calculations. The model structures 3 and 4 have been optimized in their cationic, anionic and neutral radical configurations, the results are summarized in Table I.

TABLE I Theoretical results for 3 and 4.

	$IP_{adiabatic}$ (eV)	$EA_{adiabatic}$ (eV)	$IP_{vertical}$ (eV)	$EA_{vertical}$ (eV)	$\Delta d_{N\text{-}S}^{OX}$ (Å)	$\Delta d_{N\text{-}S}^{RED}$ (Å)
3	8.62	2.82	8.69	2.66	-0.052	+0.042
4	7.80	2.72	7.80	2.52	-0.045	+0.044

The SOMO of both molecules (a_2 symmetry) is closely related to that of the 1,2,3,5 dithiadiazolyl radicals. The orbital is N-S antibonding and the central carbon atom lies on a nodal plane. Thus the electronic effect of the R substituents is expected to be small. There are also contributions to the SOMO from the other carbon atoms. IP decreases as delocalization increases from 3 to 4. This also reduces the magnitude of the changes in bond distances $\Delta d_{N\text{-}S}$ and atomic charges upon electron transfer; such features may be used to reduce intramolecular phonon contributions in a molecular conductor.

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