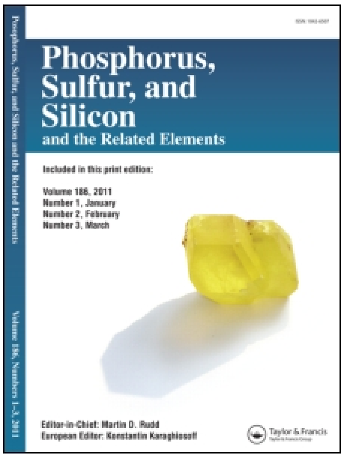

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HETEROCYCLES FROM SILYLATED AMIDINES. PREPARATION OF 1,3,2,4,6-DITHIATRIAZINES; PREPARATION AND E.S.R. CHARACTERIZATION OF NEW 1,2,3,5-DITHIA- AND DISELENADIAZOLYL RADICALS; THE CONVERSION OF DITHIADIAZOLYLS TO 1,5,2,4,6,8-DITHIATETRAZOCINES BY REACTION WITH O_2

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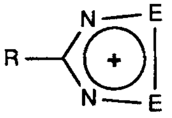
Abstract *The synthesis of 3- and 4-substituted aryl dithiatriazines,* $\{XC_6H_4CN_3S_2\}_2$, $(X = 4\text{-}CH_3, 4\text{-}Cl, 3\text{-}CF_3, 4\text{-}CF_3, 4\text{-}CH_3O, 4\text{-}C_6H_5)$; *dithiadiazolyl radicals* $4\text{-}X\text{-}C_6H_4CN_2S_2\cdot$ $(X = CH_3, CH_3O, Cl, NO_2$ *and* $CF_3)$ *and their dimers in the solid state and four new diselenadiazolyl radicals* $4\text{-}X\text{-}C_6H_4CN_2Se_2\cdot$ $(X = CH_3, CH_3O, Cl,$ *and* $CF_3)$ *as well as* $CF_3CN_2Se_2\cdot$ *and their dimers are reported. The crystal structure of the 4-Cl dithiatriazine dimer was determined. The sulphur radicals, either in bulk or in higher yield when produced in situ with* Ph_3Sb, *react with* O_2 *to give the corresponding 3- and 4-substituted 1,5,2,4,6,8-dithiatetrazocines,* $\{X\text{-}C_6H_4CN_2\}_2S_2$, $X = 4\text{-}H, 4\text{-}CH_3, 4\text{-}CH_3O, 4\text{-}Cl, 3\text{-}CF_3, 4\text{-}CF_3$. *Physical properties (mp, colour, IR and NMR data) of the derivatives with* $X = CH_3$ *and* $4\text{-}CF_3$ *differ substantially from those in a previous report.*

INTRODUCTION

The dichalcogenadiazolium salts **1** and dichalcogenadiazolyl radicals **2** have recently attracted considerable attention. Salts of type **1**,E=S were first reported in 1977[1], and radicals of type **2**,E=S in 1982.[2] The corresponding Se based rings were discovered in 1989.[3] Cations of type **1**,E=S are invariably thermally robust compounds, a property consistent with their 6π aromatic character; less is known about the Se analogues.



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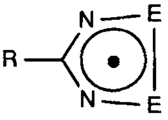

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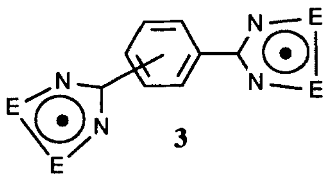

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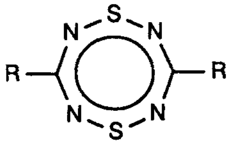

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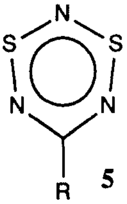
Radicals of type **2**,E=S have recently been used as ligands to transition metals, forming bimetallic complexes, *e.g.* with $Fe_2(CO)_6$, in which the free electron appears to be preserved.[4]

Diradicals of type **3** are molecular semiconductors.[5] In contrast to previously known "organic" metals, materials based on the dichalcogenadiazolyl system are not charge transfer salts, but rather assemblages of stable, interacting free-radicals, and thus represent a promising new type of synthetic material.

In view of the heightened interest in these inorganic ring systems, we have prepared and fully characterized several new compounds of type **1** and **2** with substituted aryl rings. We also report the novel conversion of type **2** radicals to 1,5,2,4,6,8-dithiatetrazocines, **4**.

Dithiatriazines **5** with two-coordinate sulphur and nitrogen atoms and a variety of substituents R have been an important but elusive class of thiazyl heterocycle.[6-9] Formally these planar rings are 8π electron systems, and thus antiaromatic. They are thus isoelectronic with the (unknown) $S_3N_3^+$ cation **6**. A variety of them have been reported,



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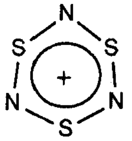

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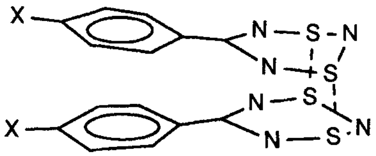

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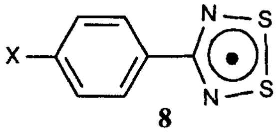
where R = CF_3 or NR_2.[6] The materials obtained have been successfully derivatized by halogens or olefins, but little is known about the parent compounds. In our initial paper on the preparation of the free dithiatriazine ring, we demonstrated that the reduction of $PhCN_3S_2$ led to a stable, insoluble, cofacial dimer, **7**.[7]

RESULTS

The synthetic methods utilized are very similar to those reported previously.[3,7] Silylated amidines were prepared according to the literature method.[10] The dithiatriazine dimers listed in the Abstract have been prepared as chemically pure crystalline solids. All have correct chemical analyses and mass spectra. The crystal structure of the 4-Cl compound was determined. It crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$ in a cell of dimensions $a = 6.107(1)$, $b = 12.070(2)$, $c = 13.206$ Å, $\alpha = 113.73(1)$, $\beta = 99.04(2)$, $\gamma = 97.53(2)°$. The least squares refinement with anisotropic thermal parameters for all non-hydrogen atoms converged at R = 0.084 for 1480 unique reflections. The structure is a cofacial dimer of $4\text{-ClC}_6H_4CN_3S_2$ units, with short S···S contacts of 2.509(4) and 2.534(4) Å. Dimer units are stacked head-to-tail in the crystal along the *bc* diagonal.

Careful NMR experiments in absolutely dry $CDCl_3$ show that these dithiatriazines dissolve to a limited extent and ***maintain the dimeric structure in solution.*** This is shown by ≈0.5 ppm shielding of the aryl protons, indicating that the face-to-face dimeric structure observed in the crystal structure is maintained in solution. There is no evidence for a monomeric dithiatriazine species in solution up to the boiling point of the solvent. The norbornene adducts of the dithiatriazines provide convenient references for the proton chemical shifts in closely related sytems, which are known by crystallography to be monomeric.

Five new dithiadiazolyls of type **8**, listed in the abstract, as well as the corresponding chloride salts have been fully characterized by mp., chemical analysis and mass spectroscopy, as well as by ESR. Four new diselenadiazolyls of type **9** have similarly been characterized, as well as $CF_3CN_2Se_2$. The ESR spectra of all the sulphur radicals (in dry toluene under Ar) have identical *g* values, and very similar hyperfine coupling constants to two equivalent ^{14}N atoms. This result is consistent with the simple molecular orbital description of these 5 membered ring systems, in which the SOMO has a node at the C atom. The Se radicals are also similar among themselves. The larger *g*-values are consistent with the greater spin-orbit coupling effect of Se. Only broad single-line signals are observed (peak→trough width of the dispersive signal 3.0-3.5 mT for the aryl derivatives; 7.5 mT for $CF_3CN_2Se_2\cdot$), consistent with the original report on $PhCN_2Se_2\cdot$.[3]



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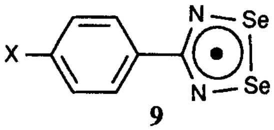

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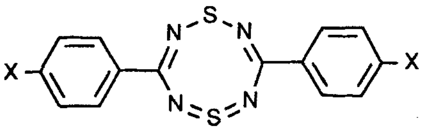
In the course of our investigation we noticed that some of the radicals, e.g. **8,X=CH_3** were extremely sensitive to trace amounts of oxygen. We therefore investigated this reaction directly. When a radical of type **8** is heated in the presence of dry O_2 in toluene or CH_3CN solution, the dark purple or black colour is slowly replaced by a lighter colour, and a light-coloured precipitate forms. NMR investigations of these initial oxidation products showed, e.g. for X=H, that a large number of products form. A persistent component of these mixtures was a yellow compound which, where X=H, CH_3O, we identified by IR (KBr disk) and mass spectroscopy as the 1,5,2,4,6,8-dithiatetrazocines, **10**.[11]



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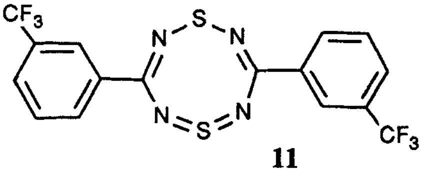

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The yields of **10** obtained, based on **2**, compared favourably with those reported by other investigators who have tried to optimize the original synthesis,[12] but are still disappointingly low (ranging from 8 to 20%). Much higher yields can be obtained by reacting the cations of type **1**,E=S directly with the Ph_3Sb reducing agent in an atmosphere of dry O_2. Yields of **10** and **11** have been realized in the range 30-60%. Moreover, in all cases chromatography was not required to purify the products, which precipitated essentially pure or contaminated by small amounts of Ph_3SbCl_2. The latter was easily separated by recrystallization from CH_3CN.

A previous paper on **10**,X=CH_3,CF_3 reports[13] significantly different physical properties for these compounds compared to what we observed. The mass spectra obtained by these workers are correct for the indicated compounds; in one case the NMR data are different, in another the IR data are different, and the reported colours and mp. of both differ greatly from those we observe. (We find yellow solids, UV-visible absorptions (X,λ_1: CH_3, 422; Cl, 414; 3-CF_3, 402; 4-CF_3, 399 nm) consistent with the planar structure determined for X = H, CH_3O.)[11] Amin and Rees have demonstrated that the reactions of benzamidine or its persilylated analogue with either SCl_2 or S_2Cl_2 leads to mixtures consisting of a large quantity of the phenyldithiadiazolium chloride, e.g. type **1** (15 to 60%) and a very small quantity of **10**,X=H (3 to 7%).[12] The reactions reported in Ref. 13 probably also lead to such mixtures.

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