[1,2,5]Selenadiazolo[3,4-*b*]pyrazines: Synthesis from 3,4-Diamino-1,2,5-selenadiazole and Generation of Persistent Radical Anions

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Abstract: Previously unknown 3,4-diamino-1,2,5-selenadiazole **6** was prepared by hydrolysis of [1,2,5]selenadiazolo[3,4-*c*][1,2,5]selenadiazole **7b** and used in synthesis of novel 1,2,5-selenadiazolo[3,4-*b*]pyrazines by the Koerner-Hinsberg reaction covering the parent compound **4** and its substituted derivatives **5a**-**g**. The compounds synthesized were characterized by solution and solid-state ^{77}Se NMR, and **6**, 5-Ph and 5,6-Me_2[1,2,5]selenadiazolo[3,4-*b*]pyrazines (**5a**,**g**, respectively) by X-ray diffraction. Electrochemical reduction of 5,6-R_2[1,2,5]selenadiazolo[3,4-*b*]pyrazines **5c**,**g** (R = Ph, Me) into novel persistent radical anions (RAs) was studied by cyclic voltammetry and the RAs [**5c**]$^-$ and [**5g**]$^-$ were characterized by EPR spectroscopy combined with DFT calculations.

Introduction

The chemistry of chalcogen-nitrogen π-heterocycles, particularly 1,2,5-chalcogenadiazoles, is an important part of contemporary organic and organoelement chemistry and its applications in the field of biomedicine and molecule-based functional materials.[1-9] Amongst 1,2,5-chalcogenadiazoles the best studied are the sulfur derivatives[1-4,7,10,11] though there are scattered reports on the selenium analogues,[2,4,7,12-14] whereas chemistry of 1,2,5-telluradiazoles is only emerging.[4-7,15,16] Very recent interest to these compounds, especially fused with benzene and heterocyclic rings, is due to their actual or potential applications as building blocks in organic functional materials such as light emitters, solar cells, synthetic metals, as well as drugs for preventive and therapeutic medical treatment and fluorescent imagine probes.[1,4,7,13,14,17]

Recently, it was shown that many classes of chalcogen-nitrogen π-heterocycles possess positive electron affinity (EA) making them suitable precursors for thermodynamically stable radical anions (RAs) which are possible building blocks for magnetically-active functional materials.[7-9] Whereas some 1,2,5-thiadiazolidyl RAs, including [1,2,5]thiadiazolo[3,4-*b*]pyrazinidyl, have already been isolated in the form of thermally stable salts,[7-9,18] investigation of their Se congeners is restricted by synthetic accessibility. There is a lack of suitable preparative approaches to many interesting and potentially useful derivatives with enlarged EA including, for example, [1,2,5]selenadiazolo[3,4-*b*]pyrazines.

In principle, these compounds could be prepared from 2,3-diaminopyrazines[19] and SeO_2, *i.e.* using the standard Hinsberg approach to the selenadiazole ring-closure.[2,4,13,14] The diamines, however, are relatively hardly accessible, and in this work two synthetic alternatives conceptually based on the Yuryev[17] and the Koerner-Hinsberg[20] reactions were investigated. The first reaction deals with heteroatom exchange in five-membered heterocycles, and the second with pyrazine ring-closure.

This paper describes the synthesis of previously unknown 3,4-diamino-1,2,5-selenadiazole and its use in the synthesis of the title compounds under conditions of the Koerner-Hinsberg reaction. The key diamine and the [1,2,5]selenadiazolo[3,4-*b*]pyrazines synthesized were characterized by multinuclear NMR including solution and solid-state ^{77}Se NMR and X-ray diffraction (XRD). The [1,2,5]selenadiazolo[3,4-*b*]pyrazines were used for electrochemical generation of their radical anions and the novel persistent RAs obtained were characterized by EPR in combination with DFT calculations.

Results and Discussion

2.1. Synthesis

Recently, the first representative of the heterocycles under discussion, *i.e.* [1,2,5]selenadiazolo[3,4-*b*]quinoxaline **1**, was obtained by direct exchange of the sulfur atom of the corresponding 1,2,5-thiadiazole **2** by a selenium atom (Scheme 1).[12]

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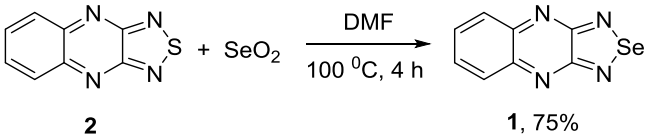
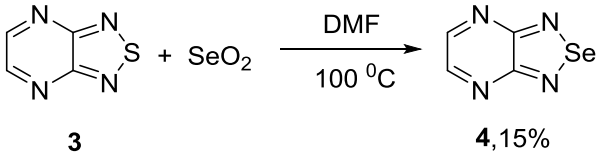
Supporting information for this article is given via a link at the end of the document.



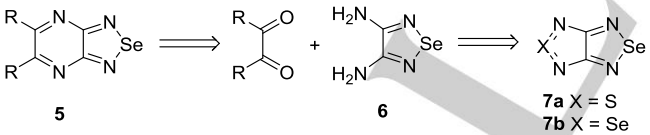
Scheme 1. Synthesis of [1,2,5]selenadiazolo[3,4-*b*]quinoxaline **1** from the corresponding thiadiazole **2**.

To explore the synthetic scope of the direct transformation of 1,2,5-thiadiazoles into 1,2,5-selenadiazoles, the reaction between [1,2,5]thiadiazolo[3,4-*b*]pyrazine **3** and SeO_2 was studied. It was found that heating **3** with SeO_2 (1.2 equiv) at 100 °C in dimethylformamide (DMF) gives [1,2,5]selenadiazolo[3,4-*b*]pyrazine **4** in low yield (Scheme 2) together with several byproducts. Attempts to purify **4** by crystallization were unsuccessful due to its instability in DMF and other organic solvents on heating.



Scheme 2. Synthesis of [1,2,5]selenadiazolo[3,4-*b*]pyrazine **4** from [1,2,5]thiadiazolo[3,4-*b*]pyrazine **3** and SeO_2.

Retrosynthetic analysis suggested that the reliable precursor of the parent [1,2,5]thiadiazolo[3,4-*b*]pyrazine **4** and its substituted derivatives **5** would be the previously unknown 3,4-diamino-1,2,5-selenadiazole **6** (Scheme 3) which can be prepared from [1,2,5]thiadiazolo[3,4-*c*][1,2,5]selenadiazole **7a** or its selenium counterpart **7b**.[12]



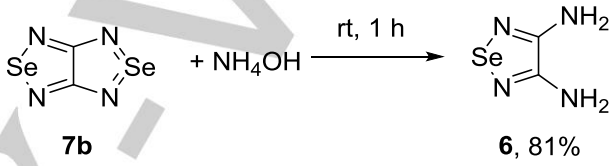
Scheme 3. Retrosynthetic route for the [1,2,5]selenadiazolo[3,4-*b*]pyrazines preparation.

1,2,5-Thia/selenadiazoles are a well-known protected form of 1,2-diamines. Normally, the diamines can be recovered by reduction of the heterocycles[21-23] and in some cases also by hydrolysis. In this work, technically simple hydrolysis was employed.

Treatment of **7a** with 3M ammonium hydroxide solution at room temperature gave no reaction whereas refluxing of the reaction for 0.5 h led to a mixture of 3,4-diamino-1,2,5-selenadiazole **6** and 3,4-diamino-1,2,5-thiadiazole **8** in practically 1 : 1 ratio (Scheme 4) suggesting that the hydrolysis rates of the thia- and selenadiazole rings of **7a** are similar under the conditions used.

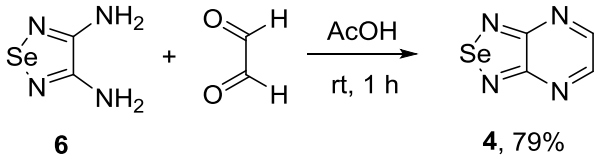
Scheme 4. Hydrolysis of [1,2,5]thiadiazolo[3,4-*c*][1,2,5]selenadiazole **7a.**

However, **7b** was easily hydrolyzed with 3M ammonium hydroxide solution to give the target compound **6** in high yield (Scheme 5). The structure of **6** was confirmed by XRD (section 2.2).



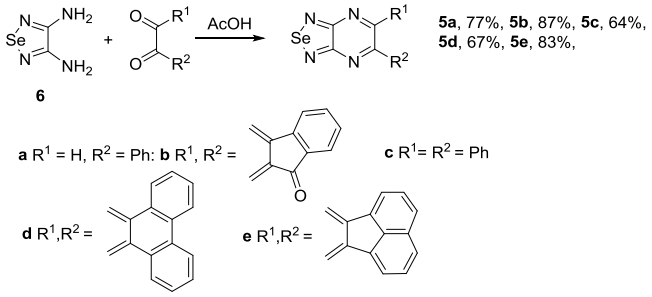
Scheme 5. Synthesis of 3,4-diamino-1,2,5-selenadiazole **6**.

Compound **6** was used in synthesis of the title compounds by the Koerner-Hinsberg reaction. With glyoxal (40% water solution), it was found that the yield of the parent selenadiazolopyrazine **4** depends strongly upon the solvent used. Refluxing in methanol and heating in ethanol at 60-65°C for 3 h gave **4** in moderate yields (53 and 51 %, respectively). Using the same reagents in glacial acetic acid for 1 h at room temperature increased the yield of **4** to 79% (Scheme 6).



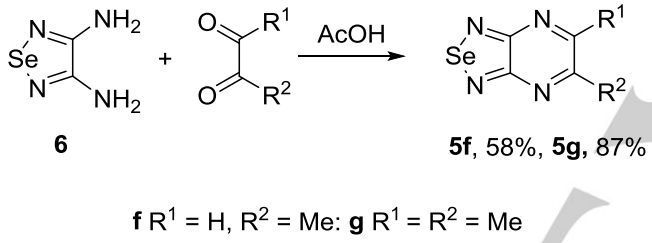
Scheme 6. Synthesis of the parent [1,2,5]selenadiazolo[3,4-*b*]pyrazine **4**.

Under the same conditions, the reaction was extended to other 1,2-diketones including fused systems with aromatic groups. With phenylglyoxal (**a**) and ninhydrine (**b**), the reaction proceeded at room temperature, though with benzyl (**c**), phenanthren-9,10-dione (**d**) and acenaphthylen-1,2-dione (**e**) refluxing in acetic acid for 3 h was required. Target products **5a-e** were obtained in moderate to high yields (Scheme 7). The structure of **5a** was confirmed by XRD (section 2.2).



Scheme 7. Synthesis of the [1,2,5]selenadiazolo[3,4-*b*]pyrazines **5a-e**.

It was found that 2-oxopropanal and diacetyl were decomposed in acetic acid, and their reaction with **6** led to complex mixtures with no significant amount of desired compounds **5**. Changing the solvent to ethanol gave better results and treatment of **6** with these diketones at room temperature for 12 h afforded derivatives **5f**,**g** in good yields (Scheme 8). The structure of **5g** was confirmed by XRD (section 2.2).



Scheme 8. Synthesis of the substituted [1,2,5]selenadiazolo[3,4-*b*]pyrazines **5f,g**.

2.2. Structure elucidation by XRD and ^{77}Se NMR

The authenticity of the compounds synthesized was confirmed by solution ^{1}H, ^{13}C and ^{77}Se NMR and XRD, and for insoluble compounds by solid-state ^{77}Se NMR.

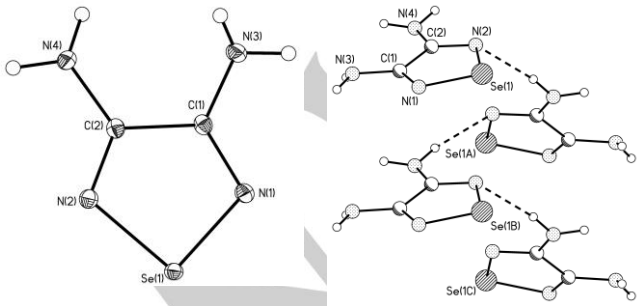


Figure 1. *ORTEP* plot of **6** showing 50% probability ellipsoids (left) and fragment of a homochiral H-bonded chain in its crystal (right).

According to XRD (Figures 1 and 2), geometries of the selenadiazole rings of **6** and **5a**,**g** are quite similar. For **6** (Figure 1), the geometry of the selenadiazole moiety is similar to that reported for 3,4-R_2-1,2,5-selenadiazoles (**9a**, R = Ph[24]; **9b**, R = CN[25]). In **5a**,**g**, the Se-N (1.786 and 1.806 Å), C-N (1.321 and 1.327 Å) and C-C (1.436 Å) distances have typical values and are statistically indistinguishable in the two compounds. In **5a,** the Ph substituent is slightly twisted out of the mean plane of the main ring with the torsion angle being 10.2°. In **5g**, the Me groups lie slightly above and below the mean plane of the ring, the torsion angle is 5.7° (Figure 2).

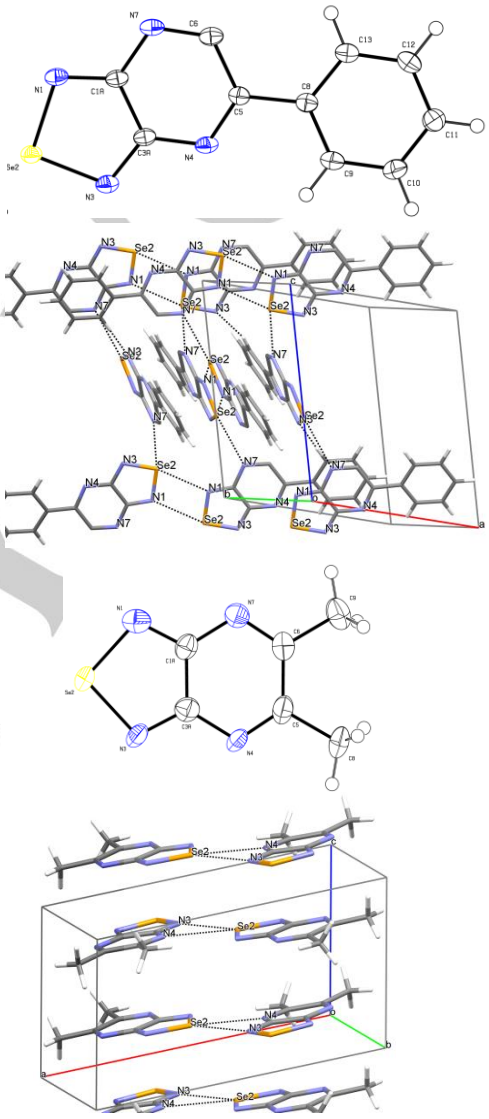


Figure 2. Left: *ORTEP* plots of **5a** (above) and **5g** (below) showing 50% probability ellipsoids. Right: Corresponding packing patterns.

In the solid state, 1,2,5-selenadiazoles normally reveal propensity to secondary bonding interactions Se…N. Those lead to 1-3 dimensional architectures via the formation of the $[Se…N]_2$ four-membered rings. The architectures are of current interest for supramolecular chemistry and crystal engineering.[26,27]

In **6**, the presence of two NH_2 groups results in an extensive H-bonded network in the crystals. The strongest N-H…N bond (N…N 3.035 Å, NHN 171°) assembles the molecules into

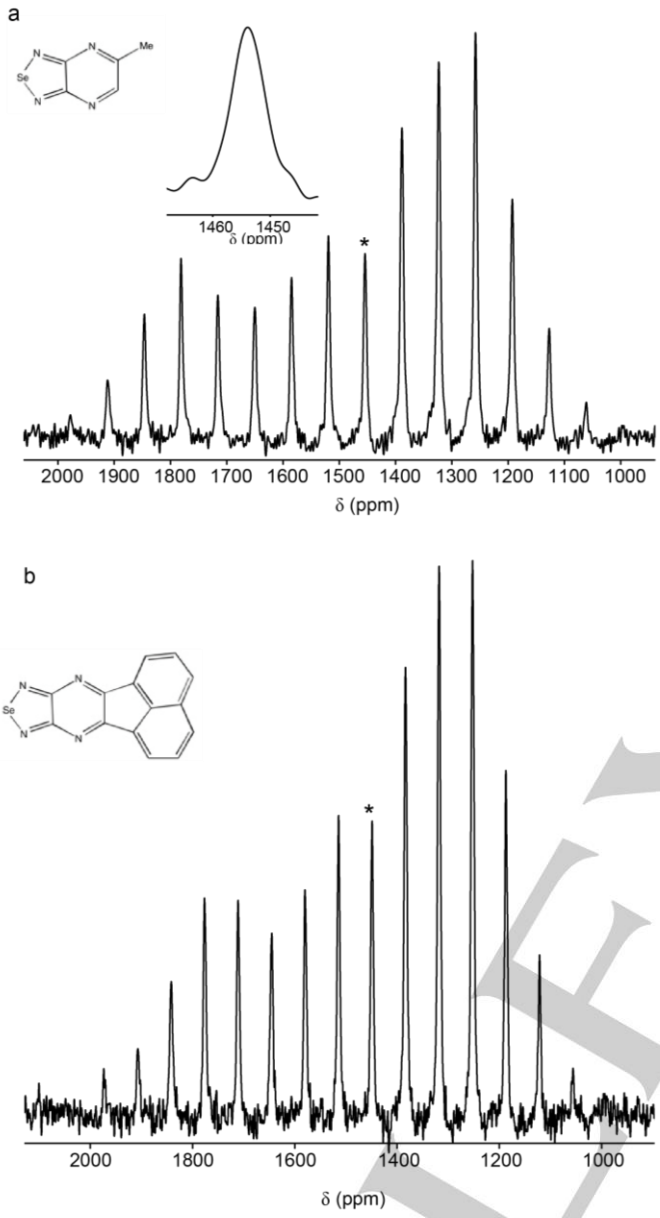


Figure 3. CP MAS ^{77}Se NMR spectra of **5f** (above) and **5e** (below) with isotropic resonances indicated by asterisks.

homochiral infinite chains (Figure 1) that interconnect via weaker N-H…N bonds (N…N 3.189–3.278 Å, NHN 128–173°) to give a non-centrosymmetric crystal packing (space group $P2_12_12_1$). There are also shortened Se…Se (3.319 Å) and Se…N (3.129 Å) contacts. In the case of **9a** these interactions give rise to centrosymmetric dimers (space group $P2_1/c$), while with **9b** they result in homochiral chains (space group $P2_12_12_1$).

In **5a**, the molecules pack the crystal in slipped herringbone fashion and these tow stacks are linked by Se...N interactions (3.022 Å) and weak N…H contacts (2.49 Å), as well as edge to face interactions of the phenyl rings. In **5g**, the molecules pack in parallel stacks along the *c* axis, the pyrazine rings lying approximately above and below each other in both stacks, with lateral contacts Se…N (3.264 Å) connecting the sheets (Figure 2). Overall, the main packing motifs are rather different in **6** and **5a**,**h**.

Cross-polarization magic angle spinning (CP MAS) ^{77}Se solid-state NMR spectra were measured for compounds **5e**,**f**. As shown in Figure 3, a single Se site was observed in both cases, consistent with the molecular symmetry, at δ_{iso} 1449 for **5e** and 1454 for **5f**. The manifold of spinning sidebands confirms the presence of a significant chemical shift anisotropy in each molecule.

The solid-state δ^{77}Se for compounds **5e**,**f** agree well with those measured in solution for compounds **5a**-**c**,**g** (δ^{77}Se, 1425-1470; Experimental). A whole set of obtained data is in accordance with the results of previous studies on similar Se-N heterocycles including 2,1,3-benzoselenadiazoles and their polyfluorinated derivatives.[12,21,28,29] For compound **6**, δ^{77}Se is 1315 thus highlighting deshielding effect of electron-withdrawing pyrazine ring in derivatives **5**.

2.3. Electrochemical properties and radical anions

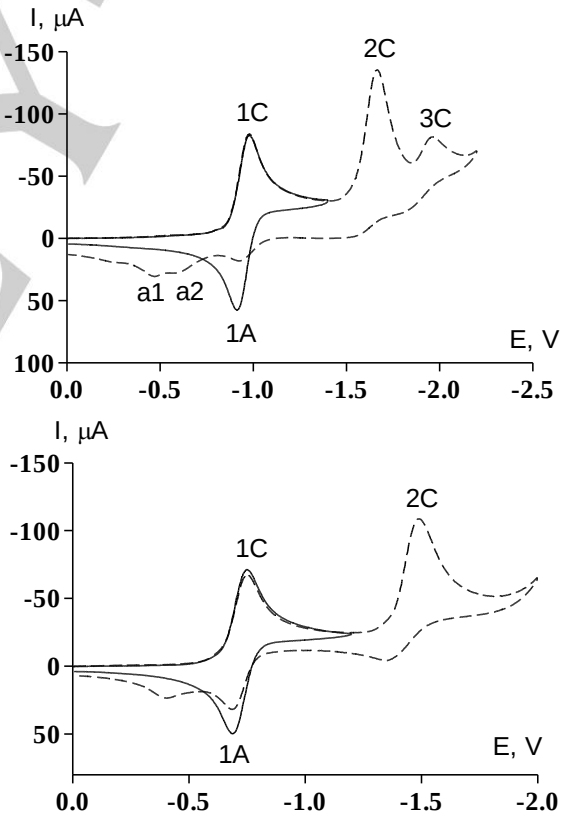


Figure 4. CV of **5g** (above) and **5c** (below) in MeCN.

Derivatives **5c** and **5g** were selected for evaluation of the potential of the title compounds for persistent RAs.

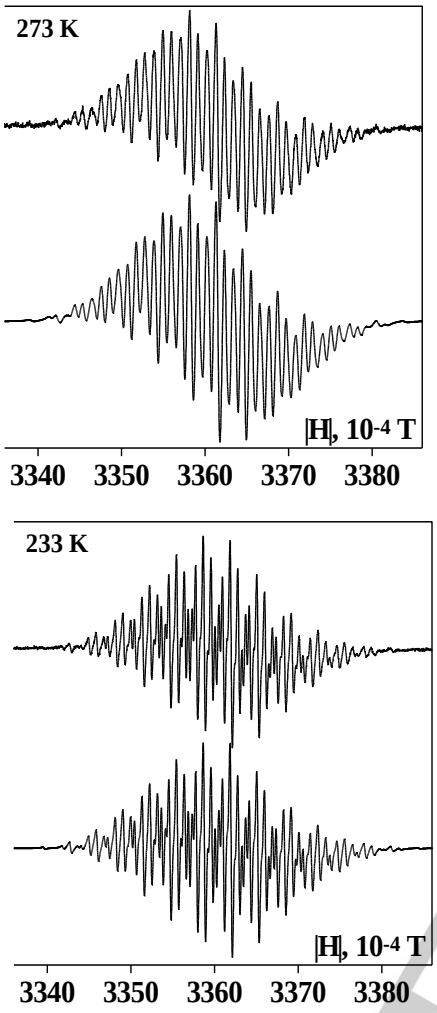


Figure 5. Experimental and simulated EPR spectra of RA [**5g**]$^{-}$.

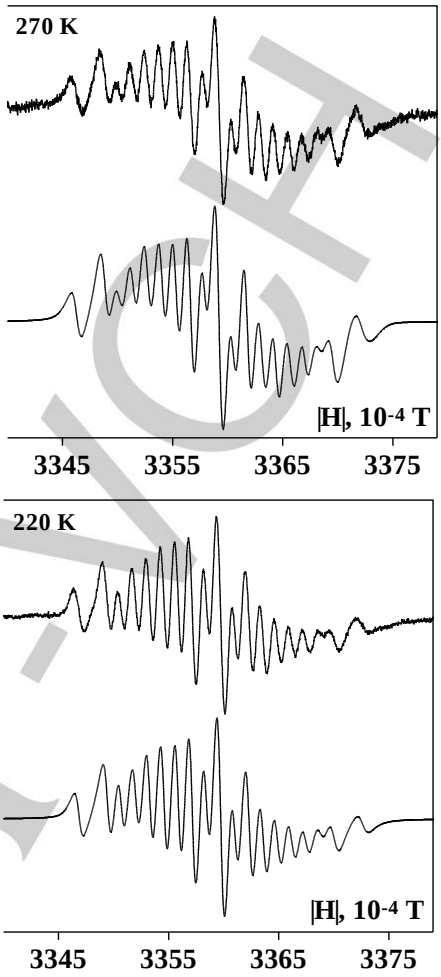


Figure 6. Experimental and simulated EPR spectra of RA [**5c**]$^{-}$.

According to the gas-phase (U)B3LYP/6-31+G(d) calculations, the first adiabatic electron affinity (EA) of compounds **5g** and **5c** are 1.55 and 1.93 eV, respectively, as compared with 0.22 eV for 1,2,5-selenadiazole and 1.06 eV for 2,1,3-benzoselenadiazole (**10**).[7]

In the potential range 0 – –2 V, the cyclic voltammogram (CV) of **5g** contains three reduction peaks E_p^{1C} = –0.98, E_p^{2C} = –1.67 and E_p^{3C} = –1.96 V, and that of **5c** two reduction peaks E_p^{1C} = –0.75 and E_p^{2C} = –1.49 V (Figure 4). For comparison, for **10** E_p^{1C} = −1.40 V.[30] For both **5g** and **5c** the first reduction peak is reversible, diffusion-controlled and one-electron (E_p^{1A} – E_p^{1C} = 0.06 V, $E_{p/2}^{1C}$ – E_p^{1C} = 0.06 V), *i.e.* corresponding to the formation of RAs [**5g**]$^{-}$ and [**5c**]$^{-}$, respectively. For both compounds the first reduction peaks are reversible even at slow potential sweep rates of 0.01 V.s^{-1} thus revealing relative stability of RAs [**5g**]$^{-}$ and [**5c**]$^{-}$. Thus, according to both CV and DFT data, compound **5c** is stronger electron acceptor than compound **5g**.

Table 1. Experimental / calculated[a] hfc constants of RAs [**5g**]$^{-}$ and [**5c**]$^{-}$.

RA	$a(N^{1,3})$, 2N	$a(N^{4,7})$, 2N	$a(H)$[b]
[**5g**]$^{-}$	0.413 / 0.401	0.228 / 0.291	0.319 / 0.317
[**5c**]$^{-}$	0.387 / 0.358	0.258 / 0.320	– [c] / 0.044, 0.040, 0.028, 0.021, 0.010

[a] UB3LYP/6-31+G(d). [b] 6H. [c] Not determined by simulation.

Electrochemical generations of RAs [**5g**]$^{-}$ and [**5c**]$^{-}$ for EPR measurements were performed in the temperature range 295–

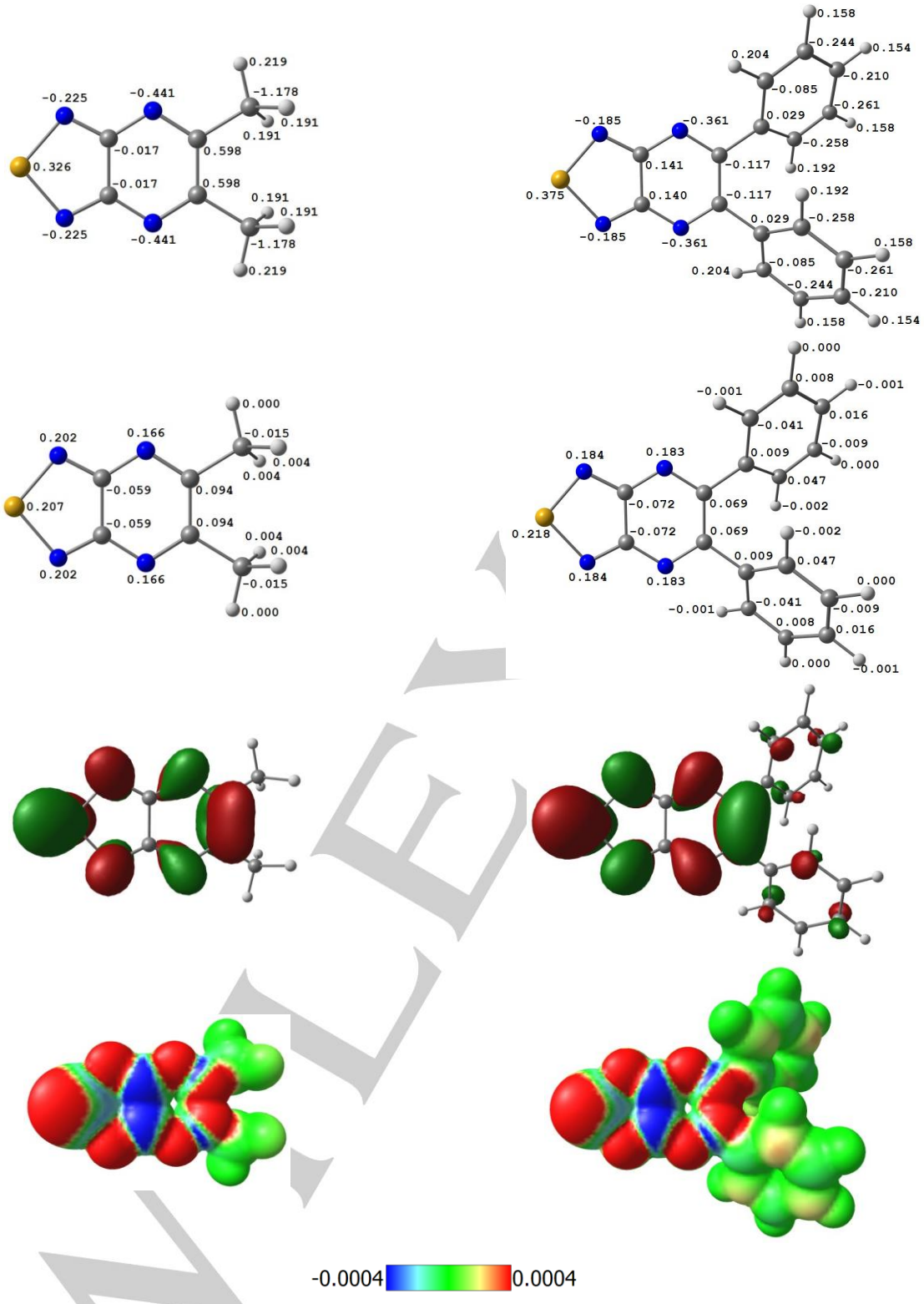


Figure 7. Top to bottom: Mulliken atomic charges, atomic spin densities, π*-SOMOs and spin density distributions on the VdW surfaces of RAs [**5g**]$^{-}$ (left) and [**5c**]$^{-}$ (right) from the UB3LYP/6-31+G(d) calculations. Color code: S – yellow, N – blue, C – grey, H – light grey.

220 K with quartz tube in the resonator shifting the spectra downfield by 145–150 G (14.5–15 mT). At 295 K, EPR spectra of only moderate quality were obtained for both RAs. Examples of low-temperature experimental spectra together with simulated ones are shown in Figures 5 and 6 for RAs [**5g**]$^-$ and [**5c**]$^-$, respectively, and the experimental and DFT-calculated hfc constants are given in Table 1. Figure 7 shows Mulliken atomic charges, atomic spin densities, π*-SOMOs and spin density distribution on the van der Waals (VdW) surfaces of RAs [**5g**]$^-$ and [**5c**]$^-$ from the UB3LYP/6-31+G(d) calculations. As follows from the calculations, the π*-SOMO in both cases is essentially antibonding. The spin density on the VdW surfaces of both RAs is mostly positive featuring negative values only in the area of C3a-C7a bond.

We anticipate that the stability of the RAs [**5c**]$^-$ and [**5g**]$^-$ under the CV conditions will lead to the eventual isolation of [1,2,5]selenadiazolo[3,4-*b*]pyrazinidyls in the form of salts after their chemical generation (*cf.* ref. 18), and this will be a direction of our further work. Due to the spin polarization of RAs (Figure 7), within the McConnell I model antiferromagnetic effects should be expected for their homospin salts where only RA is paramagnetic. For ferromagnetic effects, heterospin salts are required where both ions are paramagnetic with cations featuring negative spin density on their VdW surfaces.[7-9]

Conclusions

A convenient route to the previously unknown 3,4-diamino-1,2,5-selenadizole **6** has been developed. Compound **6** is promising starting material for variety of organic syntheses. In this work, novel [1,2,5]selenadiazolo[3,4-*b*]pyrazines including the parent compound **4** and its substituted derivatives **5a**-**g** have been prepared from **6** and 1,2-diketones by the Koerner-Hinsberg reaction. The compounds synthesized have been characterized by XRD and multinuclear NMR including ^{77}Se solid-state NMR. According to the DFT calculations, [1,2,5]selenadiazolo[3,4-*b*]pyrazines obtained possess positive EA. They are precursors of novel persistent RAs under CV conditions. The identity of the electrochemically generated RAs has been confirmed by EPR spectroscopy in combination with DFT calculations. Stability of [1,2,5]selenadiazolo[3,4-*b*]pyrazinidyls under the CV conditions motivates experiments towards their eventual isolation in the form of magnetically-active salts after chemical generation.

Experimental Section

General: Elemental analyses for C, H and N were performed with Perkin Elmer 2400 Elemental Analyser, analyses for Se by spectrophotometric method described in ref. 31. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. Solution ^{1}H (300.1 MHz), ^{13}C (75.5 MHz) and ^{77}Se (76.3 MHz) NMR spectra were taken for $CDCl_3$ solutions (unless otherwise indicated) with a Bruker AM-300 machine and referred to TMS (^{1}H and ^{13}C) and $(CH_3)_2Se$ (^{77}Se), *J* values are given in Hz. CP MAS ^{77}Se solid-state NMR experiments were performed at 298 K using a Bruker Avance III spectrometer operating at a magnetic field strength of 9.4 T corresponding to a ^{77}Se Larmor frequency of 76.3 MHz. Experiments were carried out using conventional 4 mm MAS probes and with MAS rates between 5 and 12.5 kHz. Chemical shifts are referenced relative to $(CH_3)_2Se$ at 0 ppm, using the isotropic resonance of solid H_2SeO_3 at 1288.1 ppm as a secondary reference. For all samples transverse magnetization was obtained by cross polarization from ^{1}H using optimized contact pulse durations of 40 ms, and two-pulse phase modulation ^{1}H decoupling during acquisition. Spectra were acquired with recycle intervals of between 5 and 55 s, depending on the longitudinal relaxation time of the samples. The positions of the isotropic resonances within the spinning sidebands patterns were unambiguously determined by recording a second spectrum at a higher MAS rate. MS spectra (EI, 70 eV) were obtained with a Finnigan MAT INCOS 50 instrument. High-resolution MS spectra were measured on a Bruker micrOTOF II instrument using electrospray ionization (ESI). The measurements were operated in a positive ion mode (interface capillary voltage –4500 V) or in a negative ion mode (3200 V); mass range was from m/z 50 to m/z 3000 Da; external or internal calibration was done with Electrospray Calibrant Solution (Fluka). A syringe injection was used for solutions in acetonitrile, methanol, or water (flow rate 3 μL.min^{-1}). Nitrogen was applied as a dry gas; interface temperature was set at 180°C. IR spectra were measured with a Specord M-80 instrument in KBr pellets. CV measurements on solution of compounds **5c,g** in dry MeCN (C = 2 × 10^{-3} M) were performed at 298 K in an argon atmosphere with a PG 310 USB potentiostat (HEKA Elektronik). A spherical platinum electrode (S = 0.08 cm^2) was used. The supporting electrolyte was 0.1 M Et_4NClO_4. The sweep rates were v = 0.01–1.0 V.s^{-1}. Peak potentials were quoted with reference to a saturated calomel electrode (SCE). EPR measurements on electrochemically generated RAs [**5c**]$^-$ and [**5g**]$^-$ (C = 2 mM in MeCN) were carried out with a ELEXSYS-II E500/540 spectrometer (MW power 10 mW, modulation frequency 100 kHz and modulation amplitude 0.005 mT) using a standard cell with platinum working electrode for EPR measurements under anaerobic conditions. Simulations of the experimental EPR spectra were performed with the *Winsim 2002* program[32] using the *Simplex* algorithm for many-parameter optimization of hfc values and line widths. The accuracy of calculating the hfc values was 0.001 mT. DFT calculations were performed at the (U)B3LYP/6-31+G(d) level of theory with full geometry optimization with the *Gaussian-09* program package.[33] [1,2,5]Selenadiazolo[3,4-*c*][1,2,5]selenadiazole **7b** was prepared according to the published procedure.[12]

X-ray diffraction: Crystal data for **5a**: $C_{10}H_5N_4Se$, Mr = 260.14 g mol^{-1}, monoclinic, space group $P2_1/c$, a = 14.661(3), b = 5.7089(9), c = 11.488(2) Å, β = 107.427(5), V = 917.4(3) Å^3, Z = 4, ρ_{calc} = 1.883 g m^{-3}, μ = 40.59 mm^{-1}, F(000) = 508. Rigaku XRF generator, (λ(MoKα) = 0.71072 Å), Dectris P200 detector, *T* = 173 K, 9396 reflections, 1680 independent reflections (R_{int} = 0.0361). wR2 = 0.0788 and GOF = 0.892 for all independent reflections (R1= 0.0223 was calculated against *F* for 1515 observed reflections with I > 2σ(I)). All calculations were performed using *SHELXL*.[34]

Crystal data for **5g**: $C_6H_6N_4Se$, Mr = 213.13 g mol^{-1}, monoclinic, space group $P2_1/c$, a = 12.105(8), b = 9.012(5), c = 6.811(4) Å, β = 100.059(19)°, V = 731.6(8) Å^3, Z = 4, ρ_{calc} = 1.935 g m^{-3}, μ = 50.65 mm^{-1}, F(000) = 416. Rigaku MMoo7 generator, (λ(MoKα) = 0.71072 Å), Saturn 724 detector, *T* = 125 K, 9119 reflections, 1328 independent reflections (R_{int} = 0.1008). wR2 = 0.2133 and GOF = 1.153 for all independent reflections (R1= 0.0776 was calculated against *F* for 1023 observed reflections with I > 2σ(I)). All calculations were performed using *SHELXL*.[34]

Crystal data for **6**: $C_2H_4N_4Se$, Mr = 163.05 g mol^{-1}, orthorhombic, space group $P2_12_12_1$, a = 3.93580(10), b = 8.8682(3), c = 12.8796(4) Å, V = 449.54(2) Å^3, Z = 4 (Z' = 1), ρ_{calc} = 2.409 g m^{-3}, μ = 81.98 mm^{-1}, F(000) =

312. Intensities of 9009 reflections were measured with a Bruker APEXII CCD diffractometer (λ(MoKα) = 0.71072 Å, ω-scans, θ < 58°), and 1195 independent reflections (R_{int} = 0.0215) were used in further refinement. The structure was solved by direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. Hydrogen atom positions were found in difference Fourier synthesis and refined in the isotropic approximation within the riding model. The refinement converged to wR2 = 0.0322 and GOF = 1.002 for all independent reflections (R1= 0.0119 was calculated against *F* for 1177 observed reflections with I > 2σ(I)). All calculations were performed using SHELXTL PLUS 5.0.[34]

CCDC 1401703, 1401704 and 1045610 contain the supplementary crystallographic data for **5a**, **5g** and **6**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge, CB21EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.ac.uk.

3,4-Diamino-1,2,5-selenadiazole 6: A mixture of compound **7b** (141 mg, 0.58 mmol) and a solution of NH_4OH in water (3M, 2.2 ml) was stirred at room temperature for 1 h. The reaction mixture was extracted with EtOAc (4×5 ml), washed with brine (3×10 ml) and evaporated under reduced pressure. Colorless solid, yield 0.90 g (61%). mp = 177-179ºC. Anal. calcd for $C_2H_4N_4Se$ (163.04): C 14.73, H 2.47, N 34.36. Found: C 14.52, H 2.32, N 34.65. NMR, δ, ^{1}H: 6.36 (s, 4H, $2NH_2$); ^{13}C: 153.0; ^{77}Se: 1315. IR, ν, cm^{-1}: 3420, 3278 and 3155 (NH), 1618 (C=N), 1514, 1418, 702. MS, m/z (%): 166 (M+2, 16), 164 (M^+, 100), 162 (50), 160 (20), 124 (16), 122 (90), 120 (45), 80 (33), 42 (30). ESI-MS: found *m/z* 164.9667; calc. for $C_2H_5N_4Se$ $[M+H]^+$ 164.9674.

General procedure for the reaction of 3,4-diamino-1,2,5-selenadiazole 6 with 1,2-diketones in acetic acid: A mixture of compound **6** (49 mg, 0.3 mmol) and 1,2-diketone (0.33 ммоль) in AcOH (3 ml) was stirred at room temperature for 12 h or heated under reflux for 3 h and cooled to room temperature. Precipitate was filtered off, washed by ether and dried.

[1,2,5]Selenadiazolo[3,4-*b*]pyrazine 4. Pale grey solid, yield 28 mg (61%), mp > 300°C. Anal. calcd for $C_4H_2N_4Se$ (185.05): C 25.96, H 1.09, N 30.28. Found: C 25.72, H 1.01, N 30.58. NMR (DMSO-d_6), δ, ^{13}C: 148.5, 150.8. IR, ν, cm^{-1}: 1479, 1395, 1254, 1168, 1008, 880, 742, 692, 521, 469. MS, m/z (%): 186 (M^+, 100), 184 (34), 107 (11), 105 (7), 80 (28), 78 (8), 45 (17), 43 (69). ESI-MS: found *m/z* 183.9442; calc. for $C_4H_2N_4{}^{78}Se$ $[M]^+$ 183.9447.

5-Phenyl[1,2,5]selenadiazolo[3,4-*b*]pyrazine 5a. Yellow solid, yield 60 mg (77%), mp 219-221°C. Anal. calcd for $C_{10}H_6N_4Se$ (185.05): C 45.99, H 2.32, N 21.45. Found: C 46.14, H 2.45, N 21.21. NMR (DMSO-d_6), δ, ^{1}H: 7.64 (m, 3H, Ph), 8.41 (m, 2H, Ph), 9.73 (s, 1H, CH); ^{13}C: 128.8, 129.8, 132.1, 135.5, 149.8, 155.2, 156.7, 157.3; ^{77}Se: 1462. IR, ν, cm^{-1}: 3062 (CH), 1552, 1482, 1274, 1215, 1030, 957, 771, 687, 507, 479. MS, m/z (%): 264 (M+2, 17), 262 (M^+, 70), 260 (61), 185 (1), 183 (27), 181 (4), 131 (7), 129 (52), 105 (15), 103 (51), 101 (11), 79 (21), 77 (11). ESI-MS: found *m/z* 284.9659; calc. for $C_{10}H_6N_4{}^{78}Se$ $[M+Na]^+$ 284.9650.

9*H*-Inden[1,2-*e*][1,2,5]selenadiazolo[3,4-*b*]pyrazin-9-one 5b. Yellow solid, yield 75 мг (87%), mp 347-349°C. Anal. calcd for $C_{11}H_4N_4OSe$ (287.14): C 46.01, H 1.40, N 19.51. Found: C 46.23, H 1.11, N 19.29. NMR (DMSO-d_6), δ, ^{1}H: 7.82 (d, 1H, Ar; *J* = 6.0), 7.98 (m, 2H, Ar), 8.22 (d, 1H, Ar; *J* = 6.0); ^{13}C: 123.8, 124.8, 134.7, 138.0, 139.7, 140.6, 155.8, 157.7, 157.8, 160.0, 188.1 (C=O); ^{77}Se: 1469. IR, ν, cm^{-1}: 3078 and 3056 (CH), 1724 (C=O), 1579, 1213, 928, 745, 480. MS, m/z (%): 290 (M+2, 8), 288 (M^+, 63), 286 (3), 132 (10), 130 (100), 128 (1), 104 (3), 102 (43), 100 (13). ESI-MS: found *m/z* 309.9441; calc. for $C_{11}H_4N_4O{}^{78}Se$ $[M+Na]^+$ 309.9443.

5,6-Diphenyl[1,2,5]selenadiazolo[3,4-*b*]pyrazine 5c. Yellow solid, yield 69 mg (64%), mp 261-263°C. Anal. calcd for $C_{16}H_{10}N_4Se$ (337.24): C 56.98, H 2.99, N 16.61, Se 23.41. Found: C 57.12, H 3.18, N 16.42, Se 23.50. NMR, δ, ^{1}H: 7.37 (m, 4H, Ph), 7.47 (m, 2H, Ph), 7.60 (m, 4H, Ph); ^{13}C: 128.3, 130.1, 130.3, 137.6, 156.5, 159.0; ^{77}Se: 1452. IR, ν, cm^{-1}: 2922 and 2852 (CH), 1659, 1579, 1393, 1277, 1211, 876, 719, 697, 642, 575, 509. MS, m/z (%): 340 (M+2, 11), 338 (M^+, 50), 336 (18), 183 (28), 129 (17), 105 (47). ESI-MS: found *m/z* 360.9960; calc. for $C_{16}H_{10}N_4{}^{78}Se$ $[M]^+$ 360.9963.

Dibenzo[*f,h*][1,2,5]selenadiazolo[3,4-*b*]quinoxaline 5d. Dark red solid, yield 40.2 mg (67%), mp > 350 °C. Anal. calcd for $C_{16}H_8N_4Se$ (335.22): C 57.33, H 2.41, N 16.71. Found: C 57.22, H 2.16, N 16.93. IR, ν, cm^{-1}: 3074 and 3056 (CH), 1601, 1450, 1330, 756, 721, 500. MS, m/z (%): 338 (M+2, 14), 336 (M^+, 92), 334 (33), 232 (10), 230 (100), 228 (1), 178 (66), 176 (86), 80 (97). ESI-MS: found *m/z* 358.9825; calc. for $C_{16}H_8N_4{}^{78}Se$ $[M+Na]^+$ 358.9807.

Acenaphtho[1,2-*e*][1,2,5]selenadiazolo[3,4-*b*]pyrazine 5e. Yellow solid, yield 77 mg (83%), mp > 350°C. Anal. calcd for $C_{14}H_6N_4Se$ (309.18): C 54.38, H 1.96, N 18.12. Found: C 54.17; H 1.88; N 17.95. NMR, δ, ^{77}Se (solid state): 1449. IR, ν, cm^{-1}: 3077 and 3055 (CH), 1610, 1421, 1210, 1110, 827, 775, 508. MS, m/z (%): 312 (M+2, 13), 310 (M^+, 67), 308 (33), 306 (13), 230 (15), 204 (100), 178 (30), 152 (33). ESI-MS: found *m/z* 332.9652; calc. for $C_{14}H_6N_4{}^{78}Se$ $[M+Na]^+$ 332.9650.

General procedure for the reaction of 3,4-diamino-1,2,5-selenadiazole 6 with 1,2-diketones in ethanol. A mixture of compound **6** (49 mg, 0.3 mmol) and 1,2-diketone (1.5 ммоль) in EtOH (3 ml) was stirred at room temperature for 12 h, the precipitate was filtered off and washed with EtOH. Combined mother liquids were evaporated under reduced pressure. The residue was triturated with ether (2 ml), precipitate was filtered, washed by ether and dried.

5-Methyl[1,2,5]selenadiazolo[3,4-*b*]pyrazine 5f. Dark red solid, yield 35 mg (58%), mp 188-190°C. Anal. calcd for $C_5H_4N_4Se$ (199.07): C 30.17; H 2.03; N 28.14. Found: C 30.34; H 1.83; N 27.96. NMR (DMSO-d_6), δ, ^{1}H: 3.35 (s, 3H, Me), 8.93 (s, 1H, Ar); ^{13}C: 23.1 (Me), 152.6(CH), 156.0, 156.9, 160.6; ^{77}Se: 1444; NMR ^{77}Se (solid state) *δ*: 1454. IR, ν, cm^{-1}: 2982 and 2937 (CH), 1625, 1526, 1356, 1092, 712, 603, 512. MS, m/z (%): 202 (M+2, 13), 200 (M^+, 100), 198 (57), 123 (4), 121 (79), 89 (4), 87 (58), 85 (23), 82 (8), 80 (62), 69 (9), 67 (76), 65 (4). ESI-MS: found *m/z* 222.9497; calc. for $C_5H_4N_4{}^{78}Se$ $[M+Na]^+$ 222.9493.

5,6-Dimethyl[1,2,5]selenadiazolo[3,4-*b*]pyrazine 5g. Yellow solid, yield 58 mg (87%), mp 205-207°C. Anal. calcd for $C_6H_6N_4Se$ (213.10): C 30.17; H 2.03; N 28.14, Se 37.05. Found: C 30.34; H 1.83; N 27.96, Se 37.15. NMR, ($CDCl_3$) δ, ^{1}H: 2.78 (s, 6H, Me); ^{13}C: 24.0, 156.4, 160.3; ^{77}Se: 1426. IR, ν, cm^{-1}: 2992 and 2956 (CH), 1479, 1395, 1254, 1168, 1008, 880, 742, 692, 521, 469. MS, m/z (%): 216 (M+2, 1), 214 (M^+, 39), 212 (18), 123 (1), 121 (54), 80 (38), 69 (4), 67 (100), 65 (16). ESI-MS: found *m/z* 236.9650; calc. for $C_6H_6N_4{}^{78}Se$ $[M+Na]^+$ 236.9650.

Acknowledgements

We gratefully acknowledge financial support from the Russian Foundation for Basic Research (Project 13-03-00072), the

Presidium of the Russian Academy of Sciences (Programme No. 8, Project 8.14) and the Leverhulme Trust (Project IN-2012-094). I.G.I, N.V.V., E.A.C. and A.V.Z. are grateful to the Ministry of Education and Science of the Russian Federation (Project of Joint Laboratories of Siberian Branch of the Russian Academy of Sciences and National Research Universities), and E.A.C. to the BP Company for postgraduate scholarship.

Keywords: synthesis • [1,2,5]selenadiazolo[3,4-*b*]pyrazines • α-diketones • 3,4-diamino-1,2,5-selenadiazole • cyclic voltammetry • EPR spectroscopy • DFT calculations • X-ray diffraction

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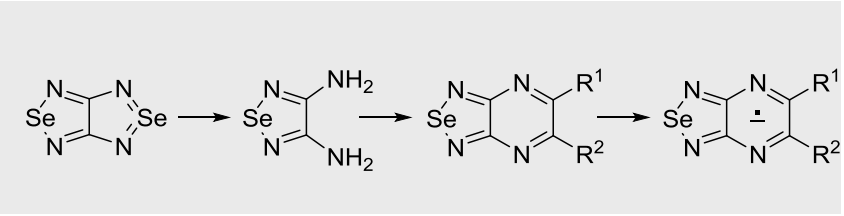

3,4-Diamino-1,2,5-selenadiazole was synthesized and used for preparing novel [1,2,5]selenadiazolo[3,4-*b*]pyrazines. Electrochemical reduction of the latter into persistent radical anions (RAs) was studied by CV and the RAs were characterized by EPR combined with DFT calculations.

Chalcogen-Nitrogen Heterocycles

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[1,2,5]Selenadiazolo[3,4-*b*]pyrazines: Synthesis from 3,4-Diamino-1,2,5-