Received: 9 July 2009,

Revised: 16 September 2009,

Published online in Wiley InterScience: 13 January 2010

(www.interscience.wiley.com) DOI 10.1002/poc.1637

Redox properties and radical anions of fluorinated 2,1,3-benzothia(selena)diazoles and related compounds

Nadezhda V. Vasilieva^a, Irina G. Irtegova^a, Nina P. Gritsan^{b,c*}, Anton V. Lonchakov^{b,c}, Alexander Yu. Makarov^a, Leonid A. Shundrin^a and Andrey V. Zibarev^{a,c**}

In comparison with 2,1,3-benzothia(selena)diazoles, electrochemical oxidation and reduction of their 4,5,6,7tetrafluoro derivatives and a number of related compounds were studied by cyclic voltammetry. For nine examples of this class, the first reduction peaks are reversible and corresponding radical anions (RAs) are long-lived at 295 K in MeCN and especially in DMF. The oxidation peaks were irreversible and corresponding radical cations were not observed. Electrochemically generated RAs were characterized by EPR measurements and DFT calculations at the UB3LYP/6-31+G(d) level. The spin density distribution in the RAs is analyzed in connection with effects of S substitution by Se and/or H by F. The prospects of the studied RAs in the design and synthesis of magnetically active materials are discussed. Copyright © 2010 John Wiley & Sons, Ltd.

Keywords: chalcogen–nitrogen π -heterocycles; cyclic voltammetry; DFT calculations; electrochemical oxidation; electrochemical reduction; EPR spectroscopy; fluorinated π -heterocycles; radical anions

INTRODUCTION

Radical ions of aromatic and heteroaromatic compounds, including polyfluorinated derivatives, are of general significance to organic chemistry and its applications.^[1-19] Radical cations (RCs) of polyfluorinated aromatics and heteroaromatics are rather stable^[6-10] and some were even isolated in the form of [AsF₆]⁻ salts.^[11] Radical anions (RAs) of polyfluorinated aromatics and heteroaromatics with one heteroatom (i.e. pentafluoropyridine) are stable in a gas phase due to positive electron affinity^[20] of their neutral precursors.^[6,21–23] They can also be isolated in solid matrices.^[6,12–19] In solution, however, these RAs are highly unstable since the negative charge is concentrated on fluorine atoms which facilitates the elimination of F⁻ anion (additional way of decay is recombination);^[6,12–19] at the same time they can be observed with some techniques, in particular with optically detected EPR.^[12,13,15,17]

The fluoride elimination can be suppressed by going from polyfluorinated aromatics to their congeners with a number of highly electronegative heteroatoms, for example, by π -isoelectronic transformation of octafluoronaphthalene into 4,5,6,7-tetrafluoro-2,1,3-benzothia(selena)diazoles (Chart 1, **3** and **4**). Such heteroatoms can effectively share negative charge with fluorine atoms to reduce its on-site values and prevent the elimination. Previous observations on the RA of **4** obtained by the reduction of the neutral precursor with elemental potassium agree with this hypothesis.^[24]

Being interested in stable π -heterocyclic RAs as the promising building blocks for magnetically active molecular materials,^[25–31] we performed the verification of the aforementioned hypothesis. In this study we report on the redox properties and radical anions of fluorinated heteroaromatics **3** and **4** and related derivatives

5–11 (Chart 1). It was found that the RAs of **3–9** are long-lived and can be characterized by EPR.

EXPERIMENTAL

Chemicals

All studied compounds (Chart 1) were prepared by described methods,^[32–36] except **10**^[37] kindly gifted by Professor R. Mews and **11** received from Alfa Aesar. Solid compounds were sublimed, and liquid compounds distilled, in vacuum directly before measurements.

DMF was distilled twice over P_2O_5 under reduced pressure, and MeCN was distilled over KMnO₄ and twice over P_2O_5 .

* Correspondence to: N. P. Gritsan, Institute of Chemical Kinetics and Combustion, Russian Academy of Sciences, 630090 Novosibirsk, Russia. E-mail: gritsan@kinetics.nsc.ru

- ** Correspondence to: A. V. Zibarev, Institute of Organic Chemistry, Russian Academy of Sciences, 630090 Novosibirsk, Russia. E-mail: zibarev@nioch.nsc.ru
- a N. V. Vasilieva, I. G. Irtegova, A. Y. Makarov, L. A. Shundrin, A. V. Zibarev Institute of Organic Chemistry, Russian Academy of Sciences, 630090 Novosibirsk, Russia
- b N. P. Gritsan, A. V. Lonchakov Institute of Chemical Kinetics and Combustion, Russian Academy of Sciences, 630090 Novosibirsk, Russia
- c N. P. Gritsan, A. V. Lonchakov, A. V. Zibarev Department of Physics, Novosibirsk State University, 630090 Novosibirsk, Russia



Chart 1.

Cyclic voltammetry

The CV measurements on degassed 2×10^{-3} M solutions of compounds **1–11** in MeCN were performed at 295 K in an argon atmosphere using CVA-1BM potentiostat equipped with a Lab-Master analog-to-digital converter with multifunctional interface (Institute of Nuclear Physics, Russian Academy of Sciences, Novosibirsk). The measurements were carried out in a mode of triangular pulse potential sweep in three-electrode electrochemical cell (V = 5 cm³) at a stationary platinum electrode (S = 8 mm²), with 0.1 M Et₄NCIO₄ as a supporting electrolyte. The sweep rates were 0.01–100 V s⁻¹, the peak potentials were quoted with reference to a saturated calomel electrode.

EPR spectroscopy

The EPR spectra were recorded on a Bruker ESP-300 spectrometer (MW power of 265 mW, modulation frequency of 100 kHz, and modulation amplitude of 0.005 mT) equipped with a rectangular double resonator and BST-100/700 temperature control unit. Unless otherwise indicated, electrochemical generation of RAs was performed at 295 K with $1-3 \times 10^{-3}$ M solutions of 1-9 in MeCN (0.1 M Et₄NClO₄ as a supporting electrolyte) in a standard cell for variable-temperature EPR measurements under anaerobic conditions equipped with stationary platinum electrode, at corresponding E_p^{1C} potentials. Numerical simulations of the experimental EPR spectra were performed with the Winsim 2002 program^[38] using Simplex algorithm for the optimization of hyperfine coupling constants (hfc) values and line widths. The accuracy in hfc calculation was ± 0.001 mT. The half-life times ($\tau_{1/2}$)

of RAs were calculated from the time dependences of the double integral intensities of EPR signals in the absence of applied potentials using the first-order kinetic equation for the RAs decay $(I = Ae^{(-kt)} + B, \tau_{1/2} = 0.69 \text{ k}^{-1})$. To minimize the longitudinal diffusion, the cell was equipped with the coaxial glass capillary located between the cathode and the anode, although the influence of the diffusion on the measured values of $\tau_{1/2}$ could not be completely excluded. The kinetic measurements were repeated at least twice, and $\tau_{1/2}$ was taken as simple average with an accuracy $\pm 5\%$. The *g* values of RAs were measured using a double resonator with Mn²⁺ in blende as standard with an accuracy of ± 0.00002 .

Quantum chemical calculation

For this work, electron affinities of neutral precursors and hyperfine coupling constants in their RAs are of special interest. They can be taken from theoretical calculations. The DFT approach at the (U)B3LYP/6-31+G(d)^[39,40] level of theory was used for the calculations since it performs well for molecular structures and properties of main-group compounds including electron affinities and hyperfine coupling constants.^[20,41,42] Previously, the (U)B3LYP method was successfully employed to reproduce the properties of a series of both closed- and open-shell chalcogen-nitrogen cycles and cages including RAs.^[25-31,43-50] Quantum chemical calculations on RAs and their neutral precursors were carried out with full geometry optimization using the GAMESS^[51] and GAUSSIAN-03^[52] programs. Note that results of calculations for the RAs do not suffer from the spin contamination effects: the expectation value of S^2 is within 0.763-0.766 for all studied RAs.

RESULTS AND DISCUSSION

The redox properties of the archetypal compounds **1** and **2** (Chart 1) and many other chalcogen–nitrogen π -heterocycles have already been studied,^[28–30,53–57] in part due to general interest to redox-active organic systems for the design and synthesis of molecular conductors and magnets. The RAs of **1** and **2** were found to be stable,^[1–5,55–57] and first of them was recently isolated in the form of [K(THF)]⁺ salt.^[25] According to the data of quantum chemical calculations and EPR spectroscopy, the RAs of **1** and **2** are π -delocalized but the spin density is substantially concentrated in the heteroatom fragment.^[25,55–57] According to our calculations, the RAs of all studied compounds are of π -type.

Cyclic voltammetry

Experimental redox potentials of compounds 1–11 are presented in Table 1. Compounds 1–11 reveal one to four reduction peaks (Table 1). Figure 1 shows the reduction cyclic voltammograms for **3** and **4** as an example. For 1–**9** the first reduction peak (1C) is one-electron, reversible ($E_p^{1A} - E_p^{1C} = 0.06 \text{ V}$, $E_{p/2}^{1C} - E_p^{1C} = 0.06 \text{ V}$), and diffusion-controlled ($l_p^{1C} \cdot v^{-1/2} = \text{const}$, where l_p^{1C} is the first

Table 1. Experimental redox potentials (V) and calculated first adiabatic electron affinities (EA ₁ , eV) of compounds 1–11 ^a					
Compound	$E_{\rm p}^{\rm 1C}~(E_{\rm p}^{\rm 2C})$	EA ₁	$E_{\rm p}^{1\rm Ox}$		
1 2 3 4 5 6 7 8 9 10	-1.56 -1.40 (-2.27) -1.21 (-2.18) ^b -1.08 (-2.02) -1.00 (-2.06) -1.37 -1.19 (-2.11) -1.17 -1.29 (-2.13) ^c -1.98 -1.72	0.861 0.978 1.570 1.670 1.911 1.235 1.419 1.504 1.669 —	2.31 2.19 2.55 2.32 2.60 2.37 2.08 2.51 2.22 		
^a In MeCN, with p and 2 were repor- ^b E_p^{3C} -2.32 V. ^c E_p^{3C} -2.22, E_p^{4C}	ootential sweep rate of 0 orted earlier. ^[54,55,57] – 2.35 V.).1 V s ⁻¹ . Poten	tials of 1		



Figure 1. CV of 3 (left) and 4 (right) at scan rates of 0.1 V s^{-1}

reduction peak current and ν is the potential sweep rate). When voltammetric cycles were switched after the first reduction peak, the ratio l_p^{1A}/l_p^{1C} was close to 1 (0.98–1.00 at $\nu = 0.1 \text{ V s}^{-1}$) for compounds **1–9** (for example, refer Fig. 1). Corresponding RAs are sufficiently stable to measure their EPR spectra under electrochemical conditions. In contrast, for compounds **10** and **11** the first reduction peak is irreversible even at sweep rates of 100 V s^{-1} .

The second reduction peak (2C) observed for compounds **2–5**, **7**, and **9** is irreversible with the sweep rates up to 100 V s^{-1} . The peak relates to further reduction of the RAs and corresponds to a transfer of two or more electrons. These transformations were beyond the scope of the present work.

Compounds **1–9** display only one diffusion-controlled (up to $\nu \le 2 \text{ V s}^{-1}$) oxidation peak (10x) which is irreversible with the sweep rates up to 100 V s⁻¹. For all compounds under study the 10x peak corresponds to a transfer of more than one electron $(l_p^{10x}/l_p^{1C} = 1.4-3.2, \text{ where } l_p^{1C} \text{ was used as a standard of one-electron transfer current, } E_p^{10x} - E_{p/2}^{10x} = 0.06-0.15 \text{ V}). Most probably, the corresponding RCs are involved in further fast transformations whose products undergo subsequent one or two electron oxidation (the fast ECE process). Monocyclic compounds$ **10**and**11**do not oxidize in the potential range up to 2.6 V.

For the bicyclic compounds **1–8** potentials of the first reduction peaks (E_p^{1C} , Table 1) correlate with corresponding gas-phase first adiabatic electron affinity (EA₁) values from the (U)B3LYP/6-31+G(d) calculations (Table 1) as EA₁ = $a(E_p^{1C}) + b$ (Fig. 2). The parameters *a*, *b*, and *r* are 1.890 eV V⁻¹, 3.823 eV, and 0.997 for S derivatives **1**, **3**, **5**, and **6**, and 2.178 eV V⁻¹, 4.028 eV, and 0.996 for Se derivatives **2**, **4**, **7**, and **8**, where *r* is the correlation coefficient. Consequently, the linear regression (Fig. 2)



Figure 2. Correlations between the EA1 and $E_{\rm p}^{\rm IC}$ values for 1–8 (white circles, S derivatives; black circles, Se derivatives)



is shifted to more negative E_p^{1C} values for S derivatives as compared with Se derivatives.

The data obtained allow discussing some structural effects in compounds **1–4**. The S derivatives **1** and **3** reveal more negative reduction potentials and more positive oxidation potentials (Table 1) than otherwise identical Se derivatives **2** and **4**. Complete substitution of the H atoms by F atoms leads to the same changes in E_p^{1C} (0.32–0.35 V) values for the corresponding pairs (**1**, **3** and **2**, **4**, as well as **9** and its hydrocarbon analog^[57]). The changes in EA₁ values (~0.7 eV) are similar for these pairs as well. Within a simplifying MO model, it indicates that this substitution does not change the type of the LUMO in both series. Previously, similar conclusion regarding the HOMO of compounds **1–4** was made on the basis of their He(I) photoelectron spectra.^[58]

EPR measurements

The electrochemically generated RAs were characterized by EPR in MeCN and DMF solutions (Table 2, Figs. 3–5). In most of the cases, the experiments were performed in MeCN which is more suitable for the chemical reduction of neutral precursors and isolation of the RAs in the form of salts planned for further research (*cf.* previous work).^[25–31] According to the half-life times (Table 2, $\tau_{1/2}$), the RAs of fluorinated derivatives, especially **4** and

9, are long-lived under the CV conditions in MeCN at 295 K. In the studied cases of RAs of **5** and **8**, $\tau_{1/2}$ values in DMF were even bigger than in MeCN. Note that the influence of diffusion on $\tau_{1/2}$ could not be completely excluded although the special precautions towards minimizing the longitudinal diffusion have been undertaken (Experimental section).

For **1**, **2**, and **4** earlier reported EPR spectra of the RAs^[24,25,55–57] are in good agreement with the data of this work. In the case of **7** only unresolved singlet was observed in both solvents. For **10** and **11**, EPR measurements were not performed due to irreversibility of their first reduction peak.

At 295 K, the spectra of Se containing RAs of **2** and **4** revealed line broadening (with line widths of 0.084 and 0.105 mT, respectively), on average by a factor 2.5 as compared with the spectra of S analogs **1** and **3**. The line broadening was also observed for RA of **8**. In part, this may be due to larger *g*-tensor anisotropy in Se containing species as evident from their *g* values which are higher than those for the S congeners (Table 2). At the same time, temperature lowering to 250 K narrowed spectral lines. This indicates additional mechanism of the line broadening at higher temperatures as a temperature-dependent (via solvent viscosity) spin-rotation relaxation.^[59] Previously, this relaxation was observed for related RAs^[27] and neutral radicals.^[50]

The experimental hfc constants (a) were assigned by comparison with the results of the UB3LYP/6-31+G(d) calcu-

Table 2. Hfc constants (mT), g values, and half-life times (s) for RAs of compounds 1-6, 8, 9, 12a,b

_	hfc Constants					
Compound	Experimental	Calculated at the UB3LYP/6-31+G(d) level	$\tau_{1/2}$	g value		
1	0.531 (N ^{1,3}), 0.261 (H ^{4,7}), 0.161 (H ^{5,6})	0.546 (N ^{1,3}), -0.381 (H ^{4,7}), -0.152 (H ^{5,6}) ^a	1990	2.00225		
2	0.594 (N ^{1,3}), 0.234 (H ^{4,7}), 0.167 (H ^{5,6}) ^b	$0.558 (N^{1,3}), -0.339 (H^{4,7}), -0.150 (H^{5,6})$	1000	2.00432		
3	0.551 (N ^{1,3}), 0.455 (F ^{4,7}), 0.455 (F ^{5,6}) ^c	0.575 (N ^{1,3}), 0.504 (F ^{4,7}), 0.249 (F ^{5,6})	135 ^d	2.00242		
4	0.613 (N ^{1,3}), 0.436 (F ^{4,7}), 0.361 (F ^{5,6}) ^e	0.581 (N ^{1,3}), 0.423 (F ^{4,7}), 0.257 (F ^{5,6})	1350	2.00363		
5	0.410 (N ¹), 0.625 (N ³), 0.692 (F ⁴),	0.402 (N ¹), 0.681 (N ³), 0.892 (F ⁴),	830	2.00239		
	0.604 (CF ₃ ⁵), 0.362 (F ⁶), 0.114 (F ⁷) ^f	0.994 (CF ₃ ⁵), -0.031 (F ⁶), 0.388 (F ⁷)				
6	0.585 (N ¹), 0.494 (N ³), 0.408 (F ⁴),	0.604 (N ¹), 0.512 (N ³), 0.520 (F ⁴), 0.176 (F ⁵),	700	2.00231		
	0.181 (F ⁵), 0.274 (H ⁶), 0.298 (H ⁷)	-0.209 (H ⁶), -0.392 (H ⁷)				
8	0.522 (N ¹), 0.607 (N ³), 0.309 (H ⁴),	0.463 (N ¹), 0.602 (N ³), -0.469 (H ⁴), 1.216 (CF ₃ ⁵),	235	2.00485		
	0.576 (CF ₃ ⁵), 0.098 (H ⁶), 0.247 (H ⁷) ^g	-0.054 (H ⁶), -0.327 (H ⁷)				
9	0.493 (N ¹), 0.533 (N ³), 0.375 (F ⁴),	0.506 (N ¹), 0.514 (N ³), 0.566 (F ⁴), 0.134 (F ⁵),	1285	2.00232		
	$0.280 (F^{5}), 0.023 (F^{6}), 0.068 (F^{7}),$	—0.057 (F ⁶), 0.175 (F ⁷), 0.395 (F ⁸), 0.240 (F ⁹)				
	$0.313 (F^8), 0.312 (F^9)^n$					
12a	0.498 (N ¹), 0.613 (N ³), 0.414 (F ⁴),	0.530 (N^{1}), 0.575 (N^{3}), 0.629 (F^{4}), 0.257 (F^{5}),	—	—		
	0.159 (F ³), 0.272 (F ⁸), 0.313 (H ⁷) ¹	0.289 (F°), -0.318 (H′)				
12b	0.613 (N ¹), 0.498 (N ³), 0.313 (F ⁴),	0.644 (N ⁻), 0.510 (N ³), 0.403 (F ⁴), 0.165 (F ³),	—	—		
	0.159 (F ³), 0.272 (H ³), 0.414 (F ²)'	-0.172 (H°), 0.583 (F′)				
^a DFT/UB3LYP/6-31G [*] : 0.535 (N ^{1,3})0.390 (H ^{4,7})0.150 (H ^{5,6}). ^[25]						
^b At 220 K: 0.596 (N ^{1,3}), 0.225 (H ^{4,7}), 0.169 (H ^{5,6}).						
^c In DMF: 0.546 (N ^{1,3}), 0.482 (F ^{4,7}), 0.478 (F ^{5,6}).						
^d For combined signal of radical anions of 3 and 12 (refer text), accuracy $\pm 20\%$. This value is not $\tau_{1/2}$ in a proper sense regarding a						
mixture of two compounds.						
^e At 215 K: 0.614 (N ^{1,3}), 0.406 (F ^{4,7}), 0.335 (F ^{5,6}).						
^f In DMF: 0.398 (N ¹), 0.623 (N ³), 0.728 (F ⁴), 0.624 (CF ₃ ⁵), 0.376 (F ⁶), 0.113 (F ⁷); $\tau_{1/2} = 2300$; $g = 2.00235$.						
^g In DMF: 0.518 (N ¹), 0.604 (N ³), 0.333 (H ⁴), 0.586 (CF ₃ ⁵), 0.096 (H ⁶), 0.269 (H ⁷); $\tau_{1/2} = 7600$; $g = 2.00507$.						
^h Tentative assignment.						
ⁱ In DMF 0.611 0.492 (14 N) 0.438 0.330 0.276 0.158 (S = $\frac{1}{2}$)						



Figure 3. EPR spectra (experiment, left; simulation, right) for a mixture of RAs of 3 and 12a,b. Top: after ~5 min of reduction (3, 70%; 12a,b, 30%). Bottom: after ~13 min of reduction (**3**, 28%; **12a,b**, 72%). H, 10⁻⁴ T

lations (Table 2). For RAs of **5**, **7**, and **8** containing CX_3 (X = H, F) groups corresponding a_X values are dynamically averaged in accordance with rapid three site exchange model, i.e. $a_k = (a_1 + a_2 + a_3)/3.$

For RA of 3 the EPR spectrum was time-dependent, i.e. further transformation of the RA was observed under the electrochemical conditions. The experimental EPR spectra were best simulated (r = 0.998, Fig. 3) as superposition of those for RAs of **3** and a product of its hydrodefluorination 12a,b (Chart 1). At the same time, it is impossible to discriminate isomers 12a and 12b on the basis of EPR and DFT data (Table 2). In DMF, this transformation proceeds more slowly than in MeCN. Thus, in DMF the ratio of integral intensities of the EPR spectra of the RAs was 82:18 in favor of **3** after \sim 70 min of electrochemical reduction,



Figure 4. EPR spectra (experiment, left; simulation, right) of RA of 4 at 215 K (top) and 290 K (bottom). H, 10⁻⁴ T



Figure 5. EPR spectra (experiment, left; simulation, right) of RAs of 5, 6, 8, 9 (top to bottom). H, 10^{-4} T

whereas in MeCN 70:30 after ~5 min of the reduction. The formation of **12a,b** most likely occurs according to the reaction routes established previously for the hydrodefluorination of RAs of polyfluorinated aromatics.^[6,60–62] The source of H atom is evidently solvent, and it is known that MeCN is a better H-donor than DMF.^[60–62] In contrast, no hydrodefluorination was observed for other studied compounds.

The data obtained make it possible to discuss the effects of S substitution by Se, and/or H by F, on spin density distribution in

the studied RAs. Overall, the calculations suggest that the spin density distribution in the RAs of **1–9** is rather similar (refer Fig. 6) which is in agreement with the experimental data. The spin density is mostly concentrated in the positions 1–3 (heterocycle) and, in the case of hydrocarbon derivatives, in the positions 4 and 7 (carbocycle). Thus, for the carbocycles of RAs of **1** and **2**, the $a_{\rm H}^{4,7}/a_{\rm F}^{5,6}$ ratio is ~1.6 and ~1.4, respectively. For their tetrafluoro derivatives **3** and **4**, the $a_{\rm F}^{4,7}/a_{\rm F}^{5,6}$ ratio is ~1.0 and ~1.2, respectively, and one can conclude that the substitution of H



Figure 6. Spin density distribution on the van der Waals surface (right column, sign color code: red $>4 \times 10^{-4}$; blue $<-4 \times 10^{-4}$; green – zero) in RAs (left column) of **1** (top), **3** (middle), and **4** (bottom) from UB3LYP/ 6-31+G(d) calculations

atoms by F ones leads to the spin density leveling within the carbocycles. In both cases this substitution practically does not affect the a_N values (Table 2), and this is also the case for RAs of **9** (Table 2) and its hydrocarbon analog.^[45] The calculations (Table 2) agree with this observation.

Substitution of the F atom in the position 5 of the RA of **5** by the CF₃ group causes redistribution of the spin density in both carboand heterocycles characterized by the a_N^1/a_N^3 ratio of ~1.5; the $a_F^4/a_F^6/a_F^7$ values relate as ~6.1:3.2:1. Similar but less pronounced effect was observed upon the substitution of the H atom in the position 5 of the RA of **8** by the CF₃ group, with the a_N^1/a_N^3 ratio of ~1.2; the $a_H^4/a_H^6/a_H^7$ values relate as ~3.2:2.5:1 (Table 2).

Calculations revealed that H substitution by F, and S by Se, practically does not change the spin density distribution in the RAs except its sign at substituents, and that the spin density on their van der Waals surfaces is mostly positive (Fig. 6). Molecular design of hetero-spin ferromagnetic salts using the discussed RAs can be performed based on the McConnell I model. This model requires positive spin density at one moiety to interact with negative spin density at another.^[63–65] Therefore, RCs with peripheral negative spin density are necessary as counter ions. Such RCs are known to be, for example, the $[Cp^*_2M]^{+*}$ ones $(Cp^* = pentamethylcyclopentadienyl, M = Cr, Mn, Fe).^[66,67]$

The approach to hetero-spin ferromagnetic RA salts can also be formulated in terms of orbital symmetry.^[68] The orthogonality of the singly occupied MOs of RA and RC of a salt favors ferromagnetic interactions, whereas non-orthogonality (strong

overlap) favors antiferromagnetic interactions. In this context RA salts with Ni²⁺ and Mn²⁺ are of special interest. Coordination numbers of transition metal cations allow coordinating more than one RA to the same metal center which favors higher Curie temperatures.^[68] Furthermore, one can expect coordination of these soft cations to the soft S (Se) centers of the RAs whereas previously studied hard Na⁺ and K⁺ cations were coordinated to the hard N centers of the RAs.^[25–31]

It is also well known that antiferromagnetic interaction between magnetic centers in combination with local spin–orbit coupling originates weak ferromagnetism by virtue of spin canting (the Dzyaloshinsky–Moriya mechanism).^[63,69,70] This stimulates further studies on heavier chalcogen RAs covering not only 2,1,3-benzoselenadiazolidyls but also their Te congeners whose neutral precursors are already described in both hydrocarbon and fluorocarbon series.^[71,72]

CONCLUSIONS

The RAs of fluorinated 2,1,3-benzothia(selena)diazoles **3** and **4** and related heterocyclic compounds **5–9** are accessible at relatively low electrochemical potentials. The identity of the RAs of **3–6**, **8**, and **9** is confirmed by EPR measurements supported by DFT calculations. At 295 K in MeCN, and especially in DMF, these RAs are long-lived under electrochemical conditions. This motivates further work toward their isolation in the form of stable salts under conditions of chemical reduction. Amongst the salts, those of Se and F containing RAs are of special interest for the design and synthesis of magnetically active materials.

For the RA of **3**, a solvent-assisted transformation into RA of **12a,b** (i.e. hydrodefluorination) was observed under electrochemical conditions. The **12a,b** specie is of the same interest to the discussed potential applications as the initial RA of **3**.

Unlike the electrochemical reduction, the first stage of the electrochemical oxidation of compounds **1–9** is irreversible and corresponds to a multiple electron transfer. The compounds **10** and **11** were not electrochemically oxidized under the experimental conditions.

Acknowledgements

The authors are grateful to Professor Yuri N. Molin for helpful discussions, and to Presidium of the Russian Academy of Sciences (Project No. 18.17), Siberian Branch of the Russian Academy of Sciences (Integration Project No. 105), and the Russian Foundation for Basic Research (Grant 07-03-00467) for financial support. Computational facilities provided by the Siberian Supercomputer Center are also gratefully acknowledged. A.V.L. appreciates the support of this work by the Russian Federal Agency of Education (Project NK-386P(3)

REFERENCES

- Z. V. Todres, *Ion-Radical Organic Chemistry: Principles and Applications*, CRC Press, Boca Raton, **2008**, pp. 478.
- [2] M. S. Denning, M. Irwin, J. Goicoechea, Inorg. Chem. 2008, 47, 6118–6120.
- [3] I. Gallardo, G. Guirado, J. Marquet, N. Vila, Angew. Chem. Int. Ed. 2007, 46, 1321–1325.
- [4] Z. V. Todres, Organic Ion Radicals. Chemistry and Applications, Marcel Dekker, Basel, 2003, pp. 464.
- [5] P. V. Schastnev, L. N. Shchegoleva, Molecular Distortions in Ionic and Excited States, CRC Press, Boca Raton, 1995, pp. 192.

- [6] V. D. Shteingarts, L. S. Kobrina, I. I. Bilkis, V. F. Starichenko, Chemistry of Polyfluoroarenes. Reaction Mechanisms and Intermediates, Nauka Publishers, Novosibirsk, 1991, pp. 181–267 (in Russian).
- [7] V. P. Vysotsky, G. E. Salnikov, L. N. Shchegoleva, Int. J. Quantum Chem. 2004, 100, 469–476.
- [8] R. D. Chambers, C. R. Sargent, M. J. Silvester, F. G. Drakesmith, J. Fluorine Chem. 1980, 15, 257–261.
- [9] J. P. Coleman, M. Fleischmann, D. Pletcher, *Electrochim. Acta* 1973, 18, 331–333.
- [10] N. M. Bazhin, N. E. Akhmetova, L. V. Orlova, V. D. Shteingarts, G. G. Yakobson, *Tetrahedron Lett.* **1968**, *9*, 4449–4452.
- [11] T. J. Richardson, F. L. Tanzella, N. Bartlett, J. Am. Chem. Soc. 1986, 108, 4937–4943.
- [12] M. M. Vyushkova, V. P. Vysotsky, I. V. Beregovaya, L. N. Shchegoleva, V. A. Bagryansky, Y. N. Molin, *Mendeleev Commun.* **2006**, *16*, 151–152.
- [13] M. M. Barlukova, I. V. Beregovaya, V. P. Vysotsky, L. N. Shchegoleva, V. A. Bagryansky, Y. N. Molin, J. Chem. Phys. A 2005, 109, 4404–4409.
- [14] I. V. Beregovaya, L. N. Shchegoleva, Int. J. Quantum Chem. 2002, 88, 481–488.
- [15] V. V. Lozovoy, V. M. Grigoryants, O. A. Anisimov, Y. N. Molin, P. V. Schastnev, L. N. Shchegoleva, I. I. Bilkis, V. D. Shteingarts, *Chem. Phys.* 1987, 112, 463–471.
- [16] L. N. Shchegoleva, I. I. Bilkis, P. V. Schastnev, Chem. Phys. 1983, 82, 343–353.
- [17] O. A. Anisimov, V. M. Grigoryants, Y. N. Molin, Chem. Phys. Lett. 1980, 74, 15–18.
- [18] M. B. Yim, S. Di Gregorio, D. E. Wood, J. Am. Chem. Soc. 1977, 99, 4260–4263.
- [19] M. B. Yim, D. E. Wood, J. Am. Chem. Soc. 1976, 98, 2053-2059.
- [20] J. C. Rienstra-Kiracofe, G. S. Tschumper, H. F. Schaefer, S. Nandi, G. B. Ellison, *Chem. Rev.* **2002**, *102*, 231–282.
- [21] Y. Xie, H. F. Schaefer, F. A. Cotton, Chem. Commun. 2003, 102.
- [22] G. W. Dillow, P. Kebarle, J. Am. Chem. Soc. 1989, 111, 5592-5596.
- [23] P. Kebarle, S. Chowhury, Chem. Rev. 1987, 87, 513-534.
- [24] J. Fajer, B. H. J. Bielski, R. H. Felton, *J. Phys. Chem.* **1968**, *72*, 1281–1288.
 [25] S. N. Konchenko, N. P. Gritsan, A. V. Lonchakov, U. Radius, A. V. Zibarev,
- Mendeleev Commun. 2009, 19, 7–9.
 [26] S. N. Konchenko, N. P. Gritsan, A. V. Lonchakov, I. G. Irtegova, R. Mews, V. I. Ovcharenko, U. Radius, A. V. Zibarev, *Eur. J. Inorg. Chem.* 2008, 3833–3838.
- [27] N. P. Gritsan, A. V. Lonchakov, E. Lork, R. Mews, E. A. Pritchina, A. V. Zibarev, *Eur. J. Inorg. Chem.* **2008**, 1994–1998.
- [28] I. Y. Bagryanskaya, Y. V. Gatilov, N. P. Gritsan, V. N. Ikorskii, I. G. Irtegova, A. V. Lonchakov, E. Lork, R. Mews, V. I. Ovcharenko, N. A. Semenov, N. V. Vasilieva, A. V. Zibarev, *Eur. J. Inorg. Chem.* **2007**, 4751–4761.
- [29] N. V. Vasilieva, I. G. Irtegova, N. P. Gritsan, L. A. Shundrin, A. V. Lonchakov, A. Y. Makarov, A. V. Zibarev, *Mendeleev Commun.* 2007, 17, 161–163.
- [30] V. N. Ikorskii, I. G. Irtegova, E. Lork, A. Y. Makarov, R. Mews, V. I. Ovcharenko, A. V. Zibarev, *Eur. J. Inorg. Chem.* **2006**, 3061–3067.
- [31] A. Y. Makarov, I. G. Irtegova, N. V. Vasilieva, I. Y. Bagryanskaya, T. Borrmann, Y. V. Gatilov, E. Lork, R. Mews, W.-D. Stohrer, A. V. Zibarev, *Inorg. Chem.* 2005, 44, 7194–7199.
- [32] A. Y. Makarov, I. Y. Bagryanskaya, F. Blockhuys, C. Van Alsenoy, Y. V. Gatilov, V. V. Knyazev, A. M. Maksimov, T. V. Mikhalina, V. E. Platonov, M. M. Shakirov, A. V. Zibarev, *Eur. J. Inorg. Chem.* **2003**, 77–88.
- [33] I. Y. Bagryanskaya, Y. V. Gatilov, A. O. Miller, M. M. Shakirov, A. V. Zibarev, *Heteroatom Chem.* **1994**, *5*, 561–565.
- [34] V. L. Salenko, M. L. Troshkov, A. V. Zibarev, J. Chromatogr. 1991, 549, 429–433.
- [35] A. V. Zibarev, A. J. Miller, J. Fluorine Chem. 1990, 50, 359-363.
- [36] A. V. Zibarev, O. M. Fugaeva, A. O. Miller, S. N. Konchenko, I. K. Korobeinicheva, G. G. Furin, *Khim. Geterotsikl. Soedin.* **1990**, 1124–1133 (in Russian; *Chem. Abstr.* 114, 100927).
- [37] M. Geisel, R. Mews, Chem. Ber. 1982, 115, 2135-2140.
- [38] D. R. Duling, J. Magn. Reson. 1994, 104, 105-110.
- [39] A. D. Becke, J. Chem. Phys. 1993, 98, 5648-5652.
- [40] C. Lee, W. Yang, R. G. Parr, Phys. Rev. B 1988, 37, 785-789.
- [41] F. Neese, Coord. Chem. Rev. 2009, 253, 526–563.

- [42] P. Geerlings, F. De Proft, W. Langenaeker, Chem. Rev. 2003, 103, 1793–1873.
- [43] E. A. Pritchina, N. P. Gritsan, A. V. Zibarev, T. Bally, *Inorg. Chem.* 2009, 48, 4075–4082.
- [44] F. Blockhuys, N. P. Gritsan, A. Y. Makarov, K. Tersago, A. V. Zibarev, Eur. J. Inorg. Chem. 2008, 655–672.
- [45] N. P. Gritsan, K. V. Shuvaev, S. N. Kim, C. Knapp, R. Mews, V. A. Bagryansky, A. V. Zibarev, *Mendeleev Commun.* 2007, 17, 204–206.
- [46] N. P. Gritsan, E. A. Pritchina, T. Bally, A. Y. Makarov, A. V. Zibarev, J. Phys. Chem. A 2007, 111, 817–824.
- [47] N. P. Gritsan, S. N. Kim, A. Y. Makarov, E. N. Chesnokov, A. V. Zibarev, *Photochem. Photobiol. Sci.* **2006**, *5*, 95–101.
- [48] A. Y. Makarov, S. N. Kim, N. P. Gritsan, I. Y. Bagryanskaya, Y. V. Gatilov, A. V. Zibarev, *Mendeleev Commun.* 2005, 15, 14–16.
- [49] N. P. Gritsan, V. A. Bagryansky, I. V. Vlasyuk, Y. N. Molin, A. Y. Makarov, M. S. Platz, A. V. Zibarev, Russ. Chem. Bull. Int. Ed. 2001, 50, 2064–2070.
- [50] I. V. Vlasyuk, V. A. Bagryansky, N. P. Gritsan, Y. N. Molin, A. Y. Makarov, Y. V. Gatilov, V. V. Shcherbukhin, A. V. Zibarev, *Phys. Chem. Chem. Phys.* 2001, *3*, 409–415.
- [51] M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguen, S. J. Su, T. L. Windus, M. Dupuis, J. A. Montgomery, J. Comput. Chem. **1993**, *14*, 1347–1363.
- [52] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian 03, Revision C.02; Gaussian, Inc.: Wallingford CT, 2004.
- [53] R. T. Boere, A. M. Bond, T. Chivers, S. W. Feldberg, T. L. Roemmele, *Inorg. Chem.* 2007, 46, 5596–5607.
- [54] R. T. Boere, T. Roemmele, Coord. Chem. Rev. 2000, 210, 369-445.
- [55] T. Suzuki, T. Tsuji, T. Okudo, A. Okada, Y. Obana, T. Fukushima, T. Miyashi, Y. Yamashita, J. Org. Chem. 2001, 66, 8954–8960.
- [56] C. L. Kwan, M. Carmack, J. K. Kochi, J. Phys. Chem. 1976, 80, 1786–1792.
- [57] N. M. Atherton, J. N. Ockwell, R. Dietz, J. Chem. Soc. A 1967, 771–777.
- [58] N. E. Petrachenko, V. I. Vovna, A. V. Zibarev, G. G. Furin, *Khim. Geterotsikl. Soedin.* **1991**, 563–567 (in Russian; Chem. Abstr. 115, 182471).
- [59] P. W. Atkins, D. Kivelson, J. Chem. Phys. 1966, 44, 169-174.
- [60] R. A. Rossi, A. B. Pierini, A. B. Penenory, Chem. Rev. 2003, 103, 71-167.
- [61] J. M. Saveant, Acc. Chem. Res. 1980, 13, 323-329.
- [62] R. A. Rossi, R. H. de Rossi, Aromatic Substitution by the SRN1 Mechanism, (Russian Translation), Mir Publishers, Moscow, 1986, 161– 189.
- [63] O. Kahn, Molecular Magnetism, VCH Publishers, New York, 1993, pp. 380.
- [64] J. J. Novoa, M. Deumal, Structure Bonding (Berlin) 2001, 100, 33-360.
- [65] H. M. McConnell, J. Chem. Phys. **1963**, 39, 1910–1917.
- [66] M. Kaupp, F. H. Koehler, Coord. Chem. Rev. 2009, 253, 2376-2386.
- [67] H. Heise, F. H. Koehler, M. Herker, W. Hiller, J. Am. Chem. Soc. 2002, 124, 10823–10832.
- [68] R. G. Hicks, Austr. J. Chem. 2001, 54, 597-600.
- [69] T. Moriya, Phys. Rev. 1960, 120, 91-98.
- [70] I. Dzyaloshinsky, J. Phys. Chem. Solids 1958, 4, 241–255.
- [71] A. F. Cozzolino, J. F. Britten, I. Vargas-Baca, Cryst. Growth Des. 2006, 6, 181–186.
- [72] V. N. Kovtonyuk, A. Y. Makarov, M. M. Shakirov, A. V. Zibarev, Chem. Commun. 1996, 1991–1992.