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Novel long-lived π-heterocyclic radical anion: a hybrid of 1,2,5-thiadiazo- and 1,2,3-dithiazolidyls

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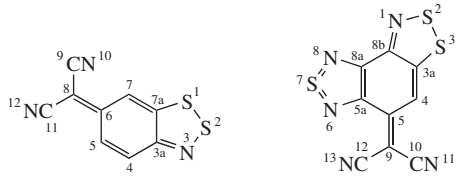
A long-lived π-heterocyclic radical anion of the hybrid 1,2,5-thiadiazolidyl/1,2,3-dithiazolidyl type was electrochemically generated and characterized by EPR spectroscopy and DFT calculations.

Chalcogen-nitrogen π-heterocycles, such as 1,2,5-thiadiazoles and their Se and Te congeners, possess high positive electron affinity (EA) and readily form radical anions (RAs) on both chemical and electrochemical reduction.[1,2] Stable salts of these RAs reveal both anti- and ferromagnetic exchange interactions in their spin systems, and they are of interest as building blocks for magnetically active molecule-based functional materials.[1,3]

1,2,3-Dithiazoles are the precursors of stable RAs.[1] Compound **1** was reduced into RA **2** (Scheme 1) isolated in the form of salts.[4] The next logical step is studying hybrid 1,2,5-thiadiazole/1,2,3-dithiazole systems.

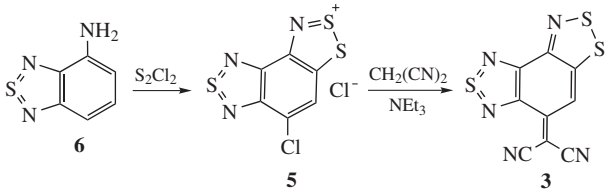


1 ($q = 0$, $S = 0$)
2 ($q = -1$, $S = 1/2$)

3 ($q = 0$, $S = 0$)
4 ($q = -1$, $S = 1/2$)

Scheme 1

According to (U)B3LYP/6-31+G(d) calculations, on going from compound **1** to compound **3**, first adiabatic EA enlarges from 2.69 to 2.74 eV (Scheme 1).† Compound **3** was synthesized by a modified method[5] *via* Herz salt **5** (Scheme 2),‡ and its structure was confirmed by XRD (Figure 1).† According to both XRD and DFT data, the molecules of compound **3** are planar.



6 **5** **3**

Scheme 2

The potential E^0 of electrochemical reduction of **3** in MeCN is –0.44 V as compared with –0.43 V for **1**[4] and 0.22 V for

† DFT calculations were performed at the (U)B3LYP/6-31+G(d) level of theory[9] with full geometry optimization with the Gaussian-09 program package.[10]

X-ray diffraction data for **3** were collected at 200 K with a Bruker Kappa Apex II CCD diffractometer with graphite-monochromatized MoKα radiation (λ = 0.71073 Å). The structure was solved with the ShelXS program and finally refined with the ShelXL program[11] using the least-squares technique. Compound **3**: $C_9HN_5S_3$, M = 275.36 g mol^{-1}, monoclinic, space group $P2_1/c$, a = 6.5299(2), b = 8.3748(3) and c = 18.7370(7) Å, β = 98.034(1)°, V = 1014.61(6) Å^3, Z = 4, d_{calc} = 1.803 g cm^{-3}, μ = 0.709 mm^{-1}, $F(000)$ = 552, crystal size 0.2×0.4×0.9 mm. Collected 19991 reflections, 2.7° < θ < 27.5°, 2116 (R_{int} = 0.034) reflections [$I > 2\sigma(I)$] used in refinement, R_1 = 0.0357, wR_2 = 0.1029, S = 1.10.

CCDC 1058868 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

Cyclic voltammetry measurements on solution of compound **2** in dry MeCN ($C \leqslant 5\times10^{-3}$ M) were performed at 298 K in an argon atmosphere with a PG 310 USB potentiostat (HEKA Elektronik). A stationary platinum electrode (S = 0.15 cm^2) was used. The supporting electrolyte was 0.1 M Et_4NClO_4. The sweep rates were v = 0.01–5.0 V s^{-1}. Peak potentials were quoted with reference to a saturated calomel electrode (SCE).

EPR measurements on electrochemically generated **4** (C = 0.73 mM in DMF) 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[12] 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. The standard equation of resonance was used to estimate the magnitude of g-factor from the values of resonance frequency and magnetic field central position.

‡ *5-Chloro[1,2,5]thiadiazolo[3,4-e][1,2,3]benzodithiazolium chloride* **5** *and 5H-[1,2,5]thiadiazolo[3,4-e][1,2,3]benzodithiazol-5-ylidenemalononitrile* **3** *(modified method)*.[5]

(*a*) At ambient temperature, 5.5 ml (66 mmol) of S_2Cl_2 were added dropwise to a stirred solution of 0.99 g (6.6 mmol) of compound **6**[13] in 5.5 ml of glacial acetic acid. The reaction mixture was stirred at ambient temperature for 3 h, at 60–70 °C for 6.5 h and cooled to room temperature. Then, 25 ml of benzene was added, and the precipitate was filtered, recrystallized from $SOCl_2$ and dried *in vacuo*. Compound **5** was obtained in the form of brown-green microcrystalline solid, 1.40 g (75 %). Found (%): C, 25.8; H, 0.5; Cl, 23.1; N, 15.1; S, 34.4. Calc. for $C_6HCl_2N_3S_3$ (%): C, 25.5; H, 0.4; Cl, 25.1; N, 14.9; S, 34.1.

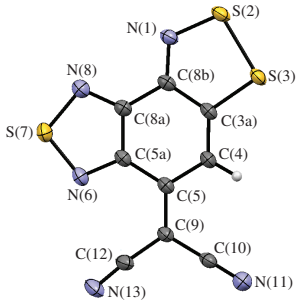


Figure 1 ORTEP plot of **3** showing 50% probability ellipsoids (H atom is shown as a circle). Selected bond lengths (Å) and bond angles (°), XRD/B3LYP/6-31+G(d): N(1)–S(2) 1.6290(19)/1.645, S(2)–S(3) 2.0861(8)/2.148, S(3)–C(3a) 1.730(2)/1.757, C(3a)–C(8b) 1.448(3)/1.467, C(8b)–N(1) 1.304(3)/1.300, C(8a)–N(8) 1.331(3)/1.323, N(8)–S(7) 1.620(2)/1.651, S(7)–N(6) 1.619(2)/1.648, N(6)–C(5a) 1.328(3)/1.326, C(5a)–C(8a) 1.426(3)/1.443, C(5)–C(9) 1.392(3)/1.392; N(1)–S(2)–S(3) 97.39(7)/97.34, S(2)–S(3)–C(3a) 93.07(7)/91.60, S(3)–C(3a)–C(8b) 112.25(14)/112.95, C(3a)–C(8b)–N(1) 120.57(19)/121.05, C(8b)–N(1)–S(2) 116.73(15)/117.07, C(5a)–N(6)–S(7) 106.34(15)/107.211, N(6)–S(7)–N(8) 100.68(11)/98.936, S(7)–N(8)–C(8a) 105.65(16)/106.489, N(8)–C(8a)–C(5a) 114.17(18)/114.319, C(8a)–C(5a)–N(6) 113.16(17)/113.046.

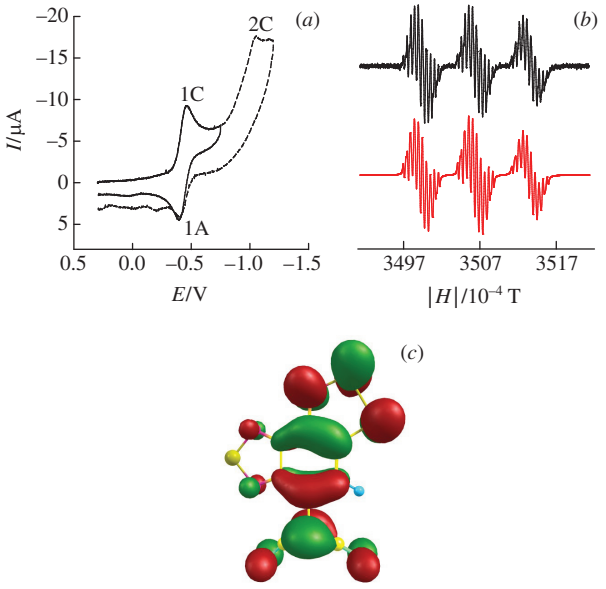


Figure 2 (*a*) Cyclic voltammogram of compound **3**, potential sweep rate 0.1 V s^{-1}. (*b*) Experimental (above) and simulated (below) EPR spectra of **4**. Experimental/UB3LYP/6-31+G(d)-calculated hfc constants (mT): 0.711/0.747 (a_N^1); 0.060/0.113 (a_N^{13}); 0.057/0.094 (a_N^{11}); 0.050/0.045 (a_N^6); 0.047/0.031 (a_N^8); 0.032/0.091 (a_H^4); g = 2.00683; *cf.* hfc constants of **2**: 0.821/0.825 (a_N^3); 0.0037/0.0084 (a_N^{10}); 0.0032/0.0078 (a_N^{12}), 0.0269/0.0281 (a_H^4); 0.010/0.0102 (a_H^5); 0.009/0.0026 (a_H^7); g = 2.01027;[4] for atom numbering, see Scheme 1. (*c*) The π*-SOMO of **4** from UB3LYP/6-31+G(d) calculations.

TCNE.[6] First reduction peak 1C (Figure 2) is reversible, diffusion-controlled and one-electron, *i.e.*, corresponding to the formation of RA **4** (Scheme 1). The RA was long-lived (half-life, 16 s) even at a slow potential sweep rate of 0.01–0.02 V s^{-1} and detected by EPR. According to DFT, the π*-SOMO of **4** is essentially

(*b*) At ambient temperature, 0.13 g (2 mmol) of malononitrile and then 0.6 ml (4 mmol) of Et_3N were added to a stirred solution of 0.56 g (2 mmol) of compound **5** in 50 ml of CH_2Cl_2. The reaction mixture was stirred for 1 h and chromatographed on a silica column with CH_2Cl_2. Violet eluate was evaporated to dryness, and compound **3** was obtained in the form of dark microcrystalline solid, 0.15 g (28%), mp > 300 °C. Found (%): C, 39.2; H, 0.4; N, 25.8; S, 35.1. Calc. for $C_9HN_5S_3$ (%): C, 39.3; H, 0.4; N, 25.4; S, 34.9. MS, *m/z*: 274.9391 $[M]^+$ (calc. for $C_9HN_5S_3$, *m/z*: 274.9389). Single crystals of **3** suitable for XRD were obtained by slow evaporating the CH_2Cl_2 solution.

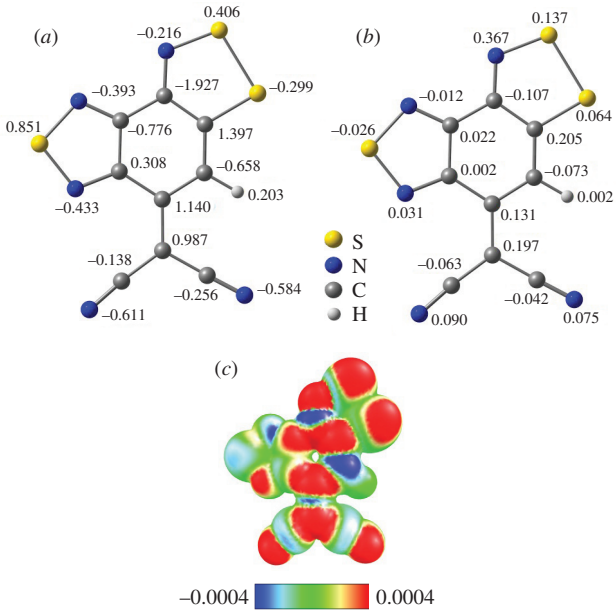


Figure 3 (*a*) Mulliken atomic charges and (*b*) spin densities of **4** from UB3LYP/6-31+G(d) calculations. (*c*) Spin density distribution on the van der Waals surface of **4** from the same calculations.

antibonding. As compared with **2**,[4] its antibonding character is enlarged due to a fused 1,2,5-thiadiazole ring (Figure 2).†

The hfc pattern of **4** resembles that of **2** (Figure 2) and differs from the pattern of 1,2,3-benzothiadiazolidyl (experiment/ UB3LYP/6-31+G(d): $a_N^{1,3}$ 0.531/0.546, $a_H^{4,7}$ 0.261/–0.381, $a_H^{5,6}$ 0.161/–0.152).[7]

According to DFT, both the spin density and the negative charge of **4** are delocalized over a whole molecule (Figure 3). As in the case of **2**,[4] spin density on the van der Waals surface of **4** is mostly positive with only small islands of negative values (Figure 3). Within the McConnell I model,[8] this means that, in the case of isolation of **4** in the form of homospin salt (where only **4** is a paramagnetic ion), antiferromagnetic interactions are anticipated, and a heterospin salt (where both ions are paramagnetic) with opposite spin polarization of ions is desired for ferromagnetic ones.[1,3,4]

Thus, hybrid 1,2,5-thiadiazolidyl/1,2,3-dithiazolidyl RA **4** was generated and characterized. Stability of **4** motivates experiments towards its eventual isolation. According to the (U)B3LYP/6-31+G(d) calculations, EA of **3** can be enlarged to 2.87 eV by the replacement of its H atom with a F atom.

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