Electronic supplementary materials *Mendeleev Commun.*, 2017, **27**, 19–22

3,1,2,4-Benzothiaselenadiazine and related heterocycles: synthesis and transformation into Herz-type radicals

Yulia M. Volkova, Alexander Yu. Makarov, Samat B. Zikirin, Alexander M. Genaev, Irina Yu. Bagryanskaya and Andrey V. Zibarev

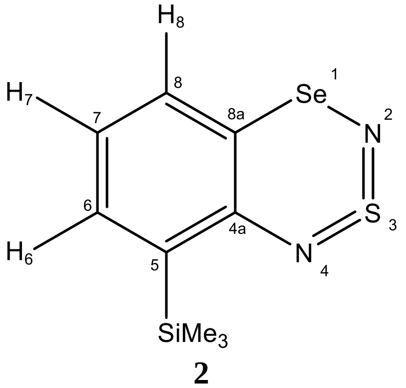
§1. Attempted syntheses of 1 with H as leaving group

Reaction between $C_6H_5N{=}S{=}NSiMe_3$[1] and $SeCl_2$[2] under conditions applied for synthesis of **1** in the present work gave a mixture whose ^{1}H NMR spectrum revealed only trace amounts of **1**. The same reaction in THF at ambient temperature gave no cyclic products.[3]

Activation of electrophilic substitution by electron-donor group, *namely*, exploiting reaction of $3\text{-}MeOC_6H_4N{=}S{=}NSiMe_3$[4] with $SeCl_2$ under conditions used in the synthesis of **1** in the present work, resulted in a mixture whose ^{1}H NMR spectrum contained signals (δ) at 6.53 (dd, 1H), 6.16 (d, 1H), 5.95 (d, 1H) and 3.67 (s, 3H) which could be assigned to 6-MeO derivative of **1**. MS spectrum of crude product revealed peak with m/z = 243.9366 ($C_7H_6ONS^{78}Se$, calculated 243.9365). However, attempts to isolate this product by vacuum sublimation were unsuccessful.

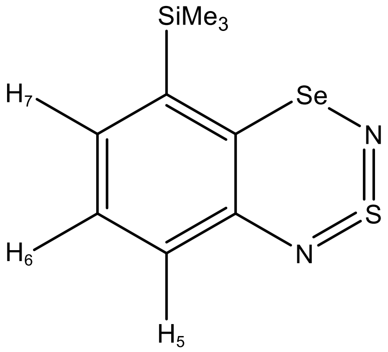
§2. Structure assignment of compounds 2 and 6

Structures of isomeric compounds **2** and **6** were assigned applying the COSY, NOESY and HMBC ^{1}H-^{1}H and ^{1}H-^{13}C NMR correlation spectroscopy techniques.



2

For **2**, signal of C_{8a} was unambiguously assigned due to coupling with ^{77}Se nucleus ($^1J_{C\text{-}Se}$ = 107.4 Hz). Long-range (7 Hz) HMBC (δ): H_6 (6.90) with C_{4a} (143.00) and C_8 (127.69), H_7 (6.94) with C_{8a} (109.04) and C_5 (134.99), H_8 (6.90) with C_8 (127.69) and C_{4a} (143.00). NOESY revealed correlation between H_6 (6.90) and protons of Me_3Si (0.18). ^1H-^1H coupling constants (COSY, Hz): H_7-H_8, 7.6; H_6-H_7, 7.5; H_6-H_8, 1.6.

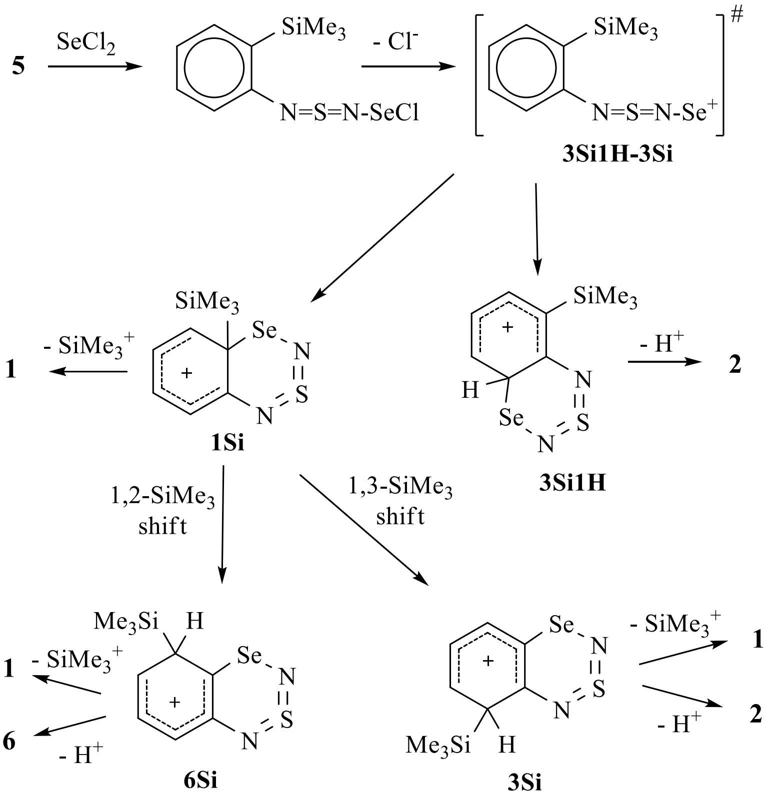


6

For **6**, long-range (7 Hz) HMBC (δ): H_5 (6.29) with C_{8a} (116.74) and C_7 (139.88), H_6 (6.81) with C_{4a} (138.67) and C_8 (139.82), H_7 (7.19) with C_{8a} (116.74) and C_5 (123.57). NOESY revealed correlation between H_7 (7.19) and protons of Me_3Si (0.25). ^1H-^1H coupling constants (COSY, Hz): H_5-H_6, 7.7; H_6-H_7, 7.5; H_5-H_7, 1.4.

§3. Me_3Si group migration during reaction of 5 with $SeCl_2$

Intramolecular migrations of Me_3Si group are well known.[5a] According to the PBE/L1 calculations,[5b,c] migration of Me_3Si group in intermediates of the reaction under discussion proceeds very easily thus explaining formation of isomeric compounds **2** and **6** (Scheme 1). The transition states and intermediates localized in the calculations are given on http://limor1.nioch.nsc.ru/quant/SeSi/. Energy parameters of all the structures are specified in Table 1.



Scheme S1 Proposed mechanism of formation of compounds **1**, **2** and **6**.

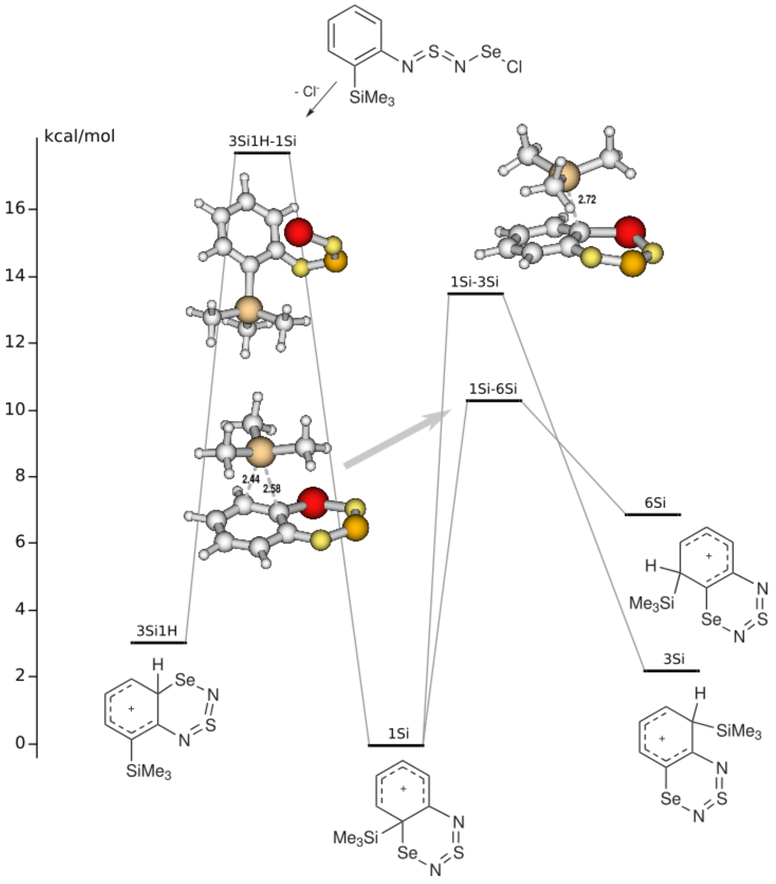


Figure S1 PBE/L1-calculated structures and relative energies of the intermediates and transition states of the reaction of **5** with $SeCl_2$.

Table S1 PBE/L1 data for the proposed mechanism of Me_3Si group migration (Scheme S1, Figure S1).

Structure	Total Energy, hartree	ZPE, hartree	Free energy correction (298.15 K), kcal mol^{-1}	D3 dispersion correction,[5d,e] kcal mol^{-1}	Relative energy with corrections, kcal mol^{-1}	Imaginary frequency, cm^{-1}
1Si-3Si	–3578.99055	0.195639	94.63	–27.66	11.6	–100.2
1Si-6Si	–3578.99568	0.196204	95.63	–26.97	10.1	–102.1
1Si	–3579.01210	0.196875	95.65	–26.76	0.0	–
3Si1H-1Si	–3578.98380	0.196012	94.83	–25.97	17.7	–63.8
3Si1H	–3579.00724	0.196850	95.16	–24.67	4.6	–
3Si	–3579.00858	0.196286	94.46	–25.4	2.4	–
6Si	–3579.00111	0.196278	94.43	–25.89	6.5	–

§4. Magnetic shielding and NICS values

^{1}H NMR spectra of **1**, **2** and **9** revealed the increased shielding of H nuclei at the positions 5 and 8 previously known for 1,3,2,4-benzodithiadiazines.[4,6] Increased shielding of ^{29}Si nuclei for **2** and **9** was not observed, as well as that for *t*-Bu group (^{1}H and ^{13}C) at the position 5 of 5,7-di-*tert*-butyl-1,3,2,4-benzodithiadizine, which is in contrast to the data for Me (^{1}H and ^{13}C) and F (^{19}F) derivatives of 1,3,2,4-benzodithiadiazine.[4,6] Replacement of S atom in the position 1 by Se one reduces this effect obviously due to weakened π-conjugation in the hetero ring. The NICS[7] values calculated at the B3LYP/6-311+(dp) level of theory for the hetero rings of 1,3,2,4-benzodithiadiazine and **1** are 14.48 and 11.72, respectively,[3] indicating reduced antiaromaticity of **1**. This is in agreement with a hypsochromic shift of the long-wave absorption in the UV-Vis spectra from 617 nm for 1,3,2,4-benzodithiadiazine[6] to 593 nm for **1** (this work).

§5. DFT calculations on radicals and simulation of their EPR spectra

For radicals **11** and **13** hfc constants were calculated by UB3LYP/6-31G(d,p) method. Combinations of B3LYP and B1B95 functionals with 6-31G(d) or cc-pVDZ basis sets were previously shown to reproduce a_H, a_N and a_F hfc constants of 1,2,3-benzodithiazolyls and 2,1,3-benzothiaselenazolyls fairly well, an increase of a basis set usually leads to a better reproduction of a_H constants but a worse one of a_N.[8] In this work, UB3LYP/6-31G(d,p) approach appeared to underestimate strongly the a_{Si} constant of radical **12** giving its value as 0.196 mT. For this reason for radicals **12** and **14**, the UB3LYP/TZV method, unavailable for their Se congeners **11** and **13**, was used with UB3LYP/6-31G(d,p) geometries in calculations of their hfc constants. Previously, similar combination of the UB3LYP/TZVP and UB3LYP/6-31G(d) methods was shown to perform well in a_{Si} calculations.[9]

Line widths in the EPR spectra of the radicals under discussion (mT, 3 values corresponding to 3 projections of the ^{14}N nuclear spin) are as follows: **11**: 0.291, 0.299, 0.301; **12**: 0.021, 0.023, 0.024; **14**: 0.028, 0.029, 0.029. Radical **13** is expected to reveal broad lines resembling those of radical **11**.

It is known that substitution of H atoms of 1,2,3-benzodichalcogenazolyls slightly affects the hfc constants at the unsubstituted sites, whereas g-values remain practically unchanged.[8] Therefore, it was assumed that radical **13** possesses the same or very similar g-value as its isomer **11**. In a practical sense, EPR spectra of **11** and **13** seem to be identical because broad spectral lines hide relatively small a_H^4 and a_H^7 splittings. As a result, abundance of 98.56 % indicated in Legend to Figure 2 (main text) actually represents the sum of abundances of radicals **11** (major) and **13** (minor). UB3LYP/6-31G(dp)-calculated hfc constants for **13** are (mT): a_N 0.876, a_H^4 0.417, a_H^5 0.175, a_H^6 –0.472, and a_{Si}^7 0.081.

References

1. A.V. Zibarev, A.O. Miller, Yu.V. Gatilov and G.G. Furin, *Heteroatom Chem.*, 1990, **1**, 443.
2. A. Maaninen, T. Chivers, M. Parvez, J. Pietikainen and R. Laitinen, *Inorg. Chem.,* 1999, **38**, 4093.
3. A.Yu. Makarov, K. Tersago, K. Nivesanond, F. Blockhuys, C. Van Alsenoy, M.K. Kovalev, I.Yu. Bagryanskaya, Yu.V. Gatilov, M.M. Shakirov and A.V. Zibarev, *Inorg. Chem.*, 2006, **45**, 2221.
4. I.Yu. Bagryanskaya, Yu.V. Gatilov, A.Yu. Makarov, A.M. Maksimov, A.O. Miller, M.M. Shakirov and A.V. Zibarev, *Heteroatom Chem.*, 1999, **10**, 113.
5. (a) M. Kira and T. Iwamoto, *The Chemistry of Organic Silicon Compounds*, eds. Z. Rappoport and Y. Apeloig, Wiley, 2001, vol. 3, pp. 853–948; (b) J.P. Perdew, R. Burke and M. Ernzerhof, *Phys. Rev. Lett.* 1996, **77**, 3865; (c) D.N. Laikov, *Chem. Phys. Lett.*, 2005, **416**, 116; (d) S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104;(e) S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456.
6. (a) A.Yu. Makarov, S.N. Kim, N.P. Gritsan, I.Yu. Bagryanskaya, Yu.V. Gatilov and A.V. Zibarev, *Mendeleev Commun.*, 2005, **15**, 14; (b) N.P. Gritsan, S.N. Kim, A.Yu. Makarov, E.N. Chesnokov and A.V. Zibarev, *Photochem. Photobiol. Sci.*, 2006, **5**, 95; (c) A.W. Cordes, M. Hojo, H. Koenig, M.C. Noble, R.T. Oakley and W.T. Pennington, *Inorg. Chem.*, 1986, **25**, 1137.
7. Z. Chen, C.S. Wannere, C. Corminboeuf, R. Puchta and P. von Ragué Schleyer, *Chem. Rev.*, 2005**, 105**, 3842.
8. (a) N.P. Gritsan, A.Yu. Makarov and A.V. Zibarev, *Appl. Magn. Reson.*, 2011, **4**, 449; (b) A.Yu. Makarov, F. Blockhuys, I.Yu. Bagryanskaya, Yu.V. Gatilov, M.M. Shakirov and A.V. Zibarev, *Inorg. Chem.*, 2013, **52**, 3699; (c) A.V. Pivtsov, L.V. Kulik, A.Yu. Makarov and F. Blockhuys, *Phys. Chem. Chem. Phys.*, 2011, **13**, 3873; (d) I.V. Vlasyuk, V.A. Bagryansky, N.P. Gritsan, Yu.N. Molin, A.Yu. Makarov, Yu.V. Gatilov, V.V. Shcherbukhin and A.V. Zibarev, *Phys. Chem. Chem. Phys.*, 2001, **3**, 409; (e) A.Yu. Makarov, V.V. Zhivonitko, A.G. Makarov, S.B. Zikirin, I.Yu. Bagryanskaya, V.A. Bagryansky, Yu.V. Gatilov, I.G. Irtegova, M.M. Shakirov and A.V. Zibarev, *Inorg. Chem.*, 2011, **50**, 3017.
9. L. Hermosilla, P. Calle, J. M. Garcia de la Vega and C. Sieiro, *J. Phys. Chem. A*, 2005, **109**, 7626.
10. D.R. Duling, *J. Magn. Reson.*, 1994, **104**, 105.