

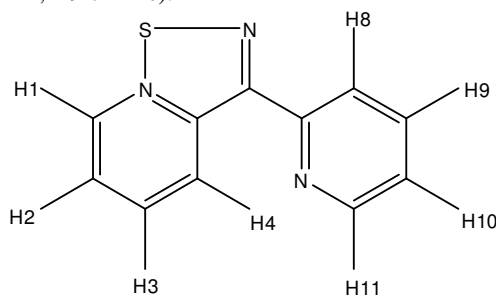
Formation of N-bridgehead 1,2,5-thiadiazolium and selenadiazolium rings through an intramolecular cyclisation reaction

Catherine E. Bacon, Dana J. Eisler, Rebecca L. Melen and Jeremy M. Rawson*

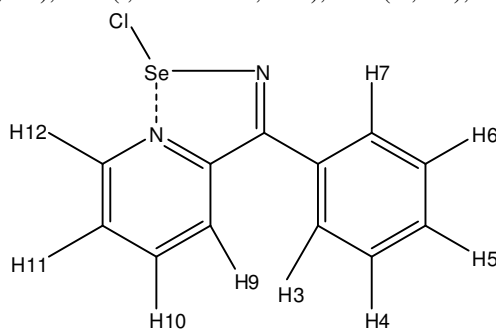
Electronic Supplementary Information: Experimental

¹H NMR assignments are tentative and based on predicted chemical shifts coupled with ¹H COSY data.

Preparation of [1]Cl. A solution of Li[N(SiMe₃)₂] (0.903 g, 5.43 mmol) in toluene (15 ml) was added to a solution of dipyrindyl ketone (1.0 g, 5.43 mmol) in toluene (15 ml) and heated to 90°C for 18h. The resultant dark red mixture was cooled to 45°C and Me₃SiCl (0.7 ml, 5.48 mol) added and stirred for 2h affording a yellow precipitate under a yellow solution. The solvent was removed *in vacuo* and the residue re-dissolved in THF (40 ml). SCl₂ (0.5 ml, 7.87 mmol) was added slowly to the reaction mixture at 0°C to generate an immediate off-white precipitate. The mixture was stirred for a further 3h, the solid separated by filtration and washed with THF (3 x 10 ml) and dried *in vacuo* (1.29 g, 95 %). This solid was recrystallised from DMF or MeOH/Et₂O as colourless needles. MS (ESI+): *m/z*(%) 214.04 (100, C₁₁H₈N₃S); Elemental Analysis [1]Cl·H₂O obs. (calc.) C 49.1 (49.4); H 3.8 (3.8); N 15.3 (15.7) %; ¹H NMR (CD₃OD): δ 10.05 (d, J = 8.40 Hz, H1); 9.99 (d, J = 6.40 Hz, H4); 8.87 (d, J = 4.00 Hz, H11); 8.60 (t, J = 8.00 Hz, H2); 8.48 (d, J = 8.00 Hz, H8); 8.10 (m, 2H (H3 and H9 or H10)); 7.64 (dd, J₁ = 7.60 Hz, J₂ = 4.80 Hz, H9 or H10).

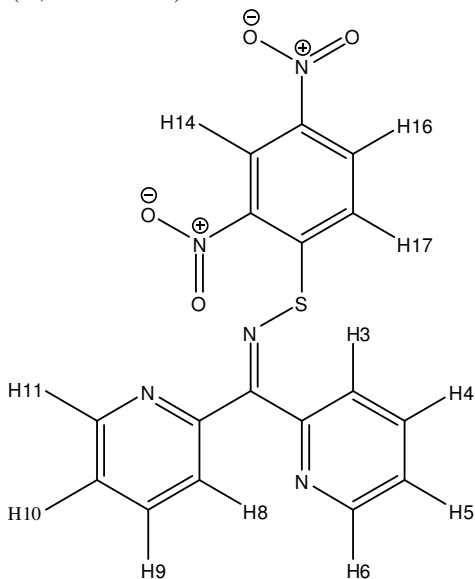


Preparation of [2]Cl. A solution of Li[N(SiMe₃)₂] (0.456 g, 2.73 mmol) in toluene (20 ml) was added to a solution of 2-benzoylpyridine (0.500 g, 2.73 mmol) in toluene (20 ml) and heated to 90°C for 18h. The dark red solution was cooled to 45°C, Me₃SiCl (0.383 ml, 3.00 mmol) added and stirred for a further 2h to generate a yellow precipitate under a yellow solution. The solvent was removed *in vacuo* and the residue re-dissolved in THF (30 ml) and cooled to 0°C. A solution of SeCl₂ (5 mmol) in THF (prepared *in situ* from SO₂Cl₂ and Se according to the literature method¹) was added slowly to form an immediate off-white solid. The mixture was stirred for a further 18h, filtered and washed with THF (3 x 10 ml). The solid was dried under reduced pressure yielding [2]Cl (0.260 g, 32 %). [2]Cl crystallised as colourless plates by slow evaporation of a DMF solution. MS (ESI+): *m/z* (%) 260.99 (100, C₁₂H₉N₂Se) plus isotope pattern; ¹H NMR (DMF-d₇): δ 9.96 (d, J = 4.50 Hz, H12); 8.65 (t, J = 7.50 Hz, H11); 8.51 (d, J = 7.00 Hz, H9); 8.17 (t, J = 6.50 Hz, H10); 8.00 (m, 2H); 7.82 (m, 3H).



1 A. Maaninen, T. Chivers, M. Perez, J. Pietikäinen, R. S. Laitinen, *Inorg. Chem.*, 1999, **38**, 4093

Preparation of 5.- A solution of dipyridylketone (0.500g, 2.71mmol) in Et₂O (15ml) was added to a solution of Li[N(SiMe₃)₂] (0.450g, 2.69mmol) in Et₂O (15ml) and stirred for 16h. Me₃SiCl (0.36ml, 2.85mmol) was added to this orange solution and stirred for 3h at room temperature. The solvent was removed *in vacuo* and the residue redissolved in CH₂Cl₂ (20ml). A solution of 2,4-(O₂N)₂C₆H₃SCl (0.68g, 2.90mmol) in CH₂Cl₂ (10ml) was added and stirred for 18h to generate a yellow precipitate of **5** which was filtered and dried *in vacuo* (0.56g, 54%). Compound **5** could be recrystallised by slow evaporation of a DMF solution at 40°C. MS (EI+) m/z (%) 382.06 (M⁺); ¹H NMR (DMF-d₇) δ 9.10 (d, J = 8.8Hz, H17); 9.03 (d, 2.4Hz, H14); 8.97 (dt, 5.2Hz, 1.2Hz, H6 or H11); 8.73 (dd, 9.2Hz, 2.4Hz, H16); 8.60 (m, H6 or H11); 8.40 (dt, 8Hz, 1.2Hz, H3 or H8); 8.08 (m, H4 and H9); 7.77 (dt, 8Hz, 1.2Hz, H3 or H8); 7.58-7.66 (m, H5 and H10).



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Electronic Supplementary Information: DFT Studies

DFT studies were undertaken on the parent derivatives **1**⁺ (R=H) and **2**⁺ (R=H) in comparison with the analogues benzothiadiazole (**3**) and benzoselenadiazole. Preliminary calculations on **1**⁺ utilised the 6-31G* basis set and B3LYP functional. However, since Se is not parameterised for 6-31G* or 6-311G* basis sets, the double-zeta valence polarised (DZVP) basis set¹ was used in conjunction with the B3LYP functional² in all subsequent calculations. All calculations and NBO analyses³ were undertaken using GAMESS-UK.⁴ All structures were geometry optimised. The geometry-optimised bond lengths and angles for **1**⁺ and **2**⁺ as well as [1]Cl and [2]Cl are shown in Figures ESI-1 and ESI-2, alongside their bond orders and partial charges derived from an NBO analysis.

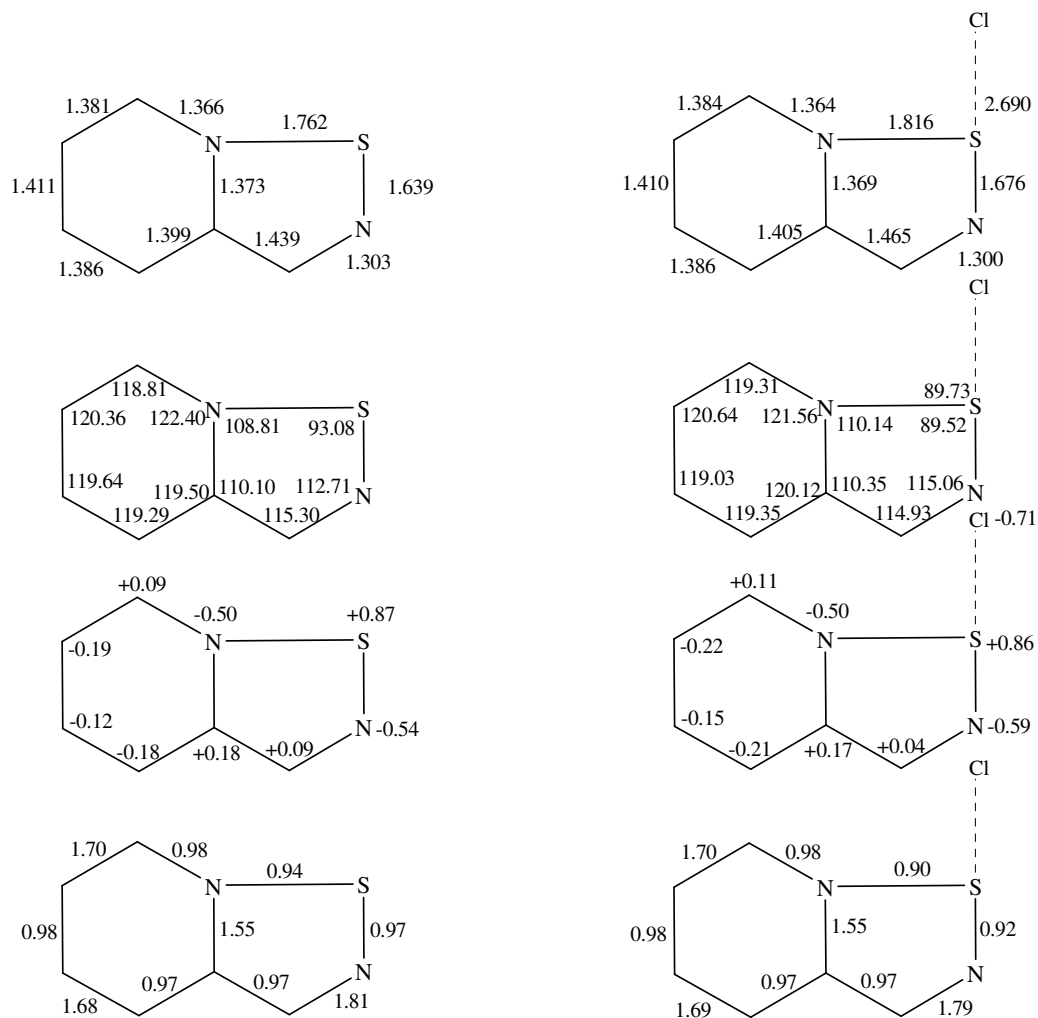


Figure ESI-1. B3LYP/DZVP geometry-optimised structures and NBO analyses of bond orders and partial charges for $1^+(R=H)$ (left) and $[1]Cl$ (R=H) (right). From top to bottom: bond lengths, bond angles, NBO charges and bond orders.

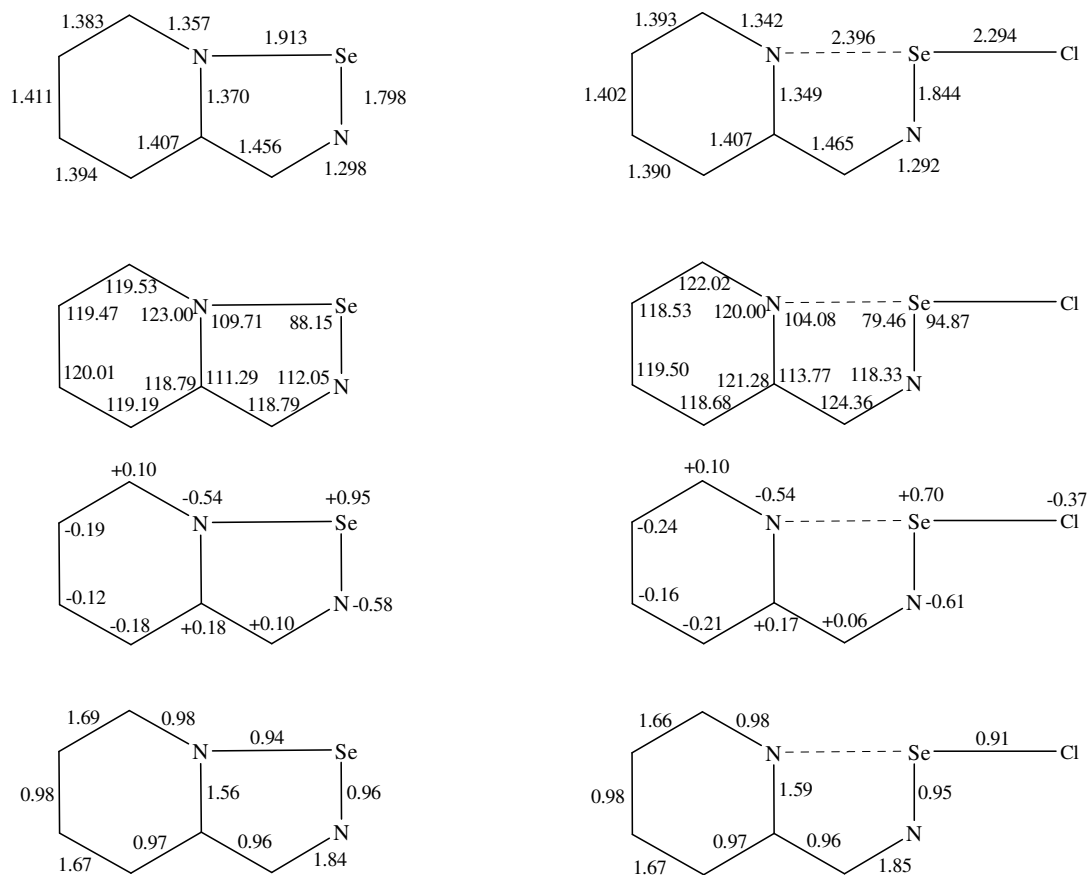


Figure ESI-2. B3LYP/DZVP geometry-optimised structures and NBO analyses of bond orders and partial charges for 2^+ (R=H) (left) and [2]Cl (R=H) (right). From top to bottom: bond lengths, bond angles, NBO charges and bond orders.

References

- 1 N. Godbout, D. R. Salahub, J. Andzelm, and E. Wimmer, *Can. J. Chem.*, 1992, **70**, 560.
- 2 A.D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B*, 1988, **37**, 785; S.H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.*, 1980, **58** 1200; P.J. Stephens, F.J. Devlin, C.F. Chabalowski, M.J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623.
- 3 A.E. Reed, L.A. Curtiss, F. Weinhold, *Chem. Rev.* 1988, **88**, 899
- 4 GAMESS-UK is a package of *ab initio* programs. See: "<http://www.cfs.dl.ac.uk/gamess-uk/index.shtml>", M.F. Guest, I. J. Bush, H.J.J. van Dam, P. Sherwood, J.M.H. Thomas, J.H. van Lenthe, R.W.A Havenith, J. Kendrick, "The GAMESS-UK electronic structure package: algorithms, developments and applications", *Mol. Phys.*, 2005, **103**, 719.