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Experimental and Theoretical Studies on 1,4,5,7-Dithiadiazepinyl Radicals: Preparation and X-ray Structure of 5-(Trimethylsilyl)tetrachlorobenzo-1,4,5,7-dithiadiazepine

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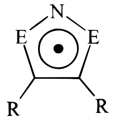
1,4,5,7-Dithiadiazepinyl radicals and their selenium analogs have been studied by density functional theory calculations. Compared to 1,2,3,5-dithiadiazolyls, this novel family of 9 π-electron radicals is predicted to have low disproportionation and dimerization energies, properties that are advantageous for the preparation of molecular conductors. The radical $[CH_3C_6H_3S_2N_2C(C_6H_4CH_3\text{-}4)]^{\bullet}$ (**5a**) was generated in solution by the cyclocondensation reaction of $CH_3C_6H_3(SCl)_2$ with $4\text{-}CH_3C_6H_4CN_2(SiMe_3)_3$ followed by treatment with PhSeCl. The ESR spectrum of **5a** consists of a slightly asymmetric quintet ($g = 2.0070$ and $A_N(\text{iso}) = 4.9$ G). The *N*-(trimethylsilyl)-substituted precursor $\overline{S(C_6Cl_4)S(NSiMe_3)(4\text{-}CH_3C_6H_4C){=}N}$ (**6c**) was characterized by X-ray crystallography: monoclinic, $P2_1/a$, $a = 12.585(3)$ Å, $b = 12.211(2)$ Å, $c = 14.003(2)$ Å, $\beta = 101.86(2)°$, $V = 2106.0(7)$ Å^3, and $Z = 4$. Polycyclocondensation reactions and thermal instability toward elimination of nitriles hamper the isolation of pure samples of the radicals.

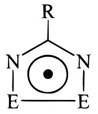
Introduction

The sulfur−nitrogen combination is able to stabilize electron-rich systems as well as open-shell species. The latter is especially true when the unpaired electron resides in the π framework of a molecule.[1] A number of SN-containing cyclic and acyclic radicals have been studied in recent years. Some of these species are stable for limited periods of time and can only be observed as transient intermediates in the decay or rearrangement of other SN compounds, e.g. $(ArS)_2N^{\bullet}$ [2] and $RC(NSAr)_2^{\bullet}$ (**1**).[3,4] On the other hand, there are radicals that are stable in solution indefinitely, which can be isolated in the solid state either as the corresponding dimers, e.g. 1,3,2-dithiazolyl radicals (**2**),[5] or, in some exceptional cases, as unassociated paramagnetic species, e.g. $[2,4,6\text{-}(C_6H_5)_3C_6H_2\text{-}NS\text{-}C_6H_4Cl\text{-}4]^{\bullet}$ [6] and $4\text{-}NCC_6F_4CN_2S_2^{\bullet}$ (**3c**).[7]



2a, E= S, R = H

2b, E= Se, R = H



3a, E= S, R = H

3b, E= Se, R = H

3c, E= S, R = 4-NCC$_6$F$_4$

The interest in this area has been fueled, in part, by the possibility of employing cyclic radical "plates" for the construction of molecular conductors,[8] as an alternative to charge-transfer salts. The progress achieved has been remarkable. An extensive family of dithiadiazolyl radicals (**3**) and their selenium analogs has been studied.[9] While the first derivatives prepared behaved as semiconductors,[10] bis(dithiadiazolyl) biradicals doped with iodine have recently attained metallic values of conductivity.[11] Uniform radical stacking and enhanced intercolumnar interactions are responsible for the increase in conductivity. Further improvement may come from the use of other families of radicals. In particular, larger ring radicals are attractive since they may spread electron density over a more extensive area and, in this way, reduce the interelectronic repulsions and provide better conductors. However, few six-membered cyclic SN radicals have been studied[12] and there is only one eight-membered ring radical known.[13]

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(1) Preston, K. F.; Sutcliffe, L. H. *Mag. Reson. Chem.* **1990**, *28*, 189.

(2) (a) Lecher, H.; Kökerle, K.; Stocklin, P. *Chem. Ber.* **1925**, *58*, 423. (b) Miura, Y.; Makita, N.; Kinoshita, M. *Tetrahedron Lett.* **1975**, *2*, 127. (c) Miura, Y.; Makita, N.; Kinoshita, M. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 482. (d) Harrison, S. R.; Pilkington, R. S.; Sutcliffe, L. H. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 669. (e) Mayer, R.; Decker, D.; Bleisch, S.; Domschke, G. *J. Prakt. Chem.* **1987**, *329*, 81.

(3) Chandrasekhar, V.; Chivers, T.; Kumaravel, S. S.; Parvez, M.; Rao, M. N. S. *Inorg. Chem.* **1991**, *30*, 4125.

(4) Chivers, T.; McGarvey, B.; Parvez, M.; Vargas-Baca, I.; Ziegler, T. *Inorg. Chem.* **1996**, *35*, 3839.

(5) (a) Awere, E. G.; Burford, N.; Haddon, R. C.; Parsons, S.; Passmore, J.; Waszczak, J. V.; White, P. S. *Inorg. Chem.* **1990**, *29*, 4821. (b) Wolmershäuser, G.; Kraft, G. *Chem. Ber.* **1990**, *123*, 881.

(6) Miura, Y.; Tanaka, A. *J. Chem. Soc., Chem. Commun.* **1990**, 441.

(7) Banister, A. J.; Bricklebank, N.; Lavender, I.; Rawson, J. M.; Gregory, C. I.; Tanner, B. K.; Clegg, W.; Elsegood, M. R. J.; Palacio, F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2533.

(8) (a) Haddon, R. C. *Nature* **1975**, *256*, 394. (b) Haddon, R. C. *Aust. J. Chem.* **1975**, *28*, 2343.

(9) (a) Oakley, R. T. *Can. J. Chem.* **1993**, *71*, 1775. (b) Bryan, C. D.; Cordes, A. W.; Fleming, R. M.; George, N. A.; Glarum, S.H.; Haddon, R. C.; Oakley, R. T.; Palstra, T. T. M.; Perel, A. S.; Schneemeyer, L. F.; Waszczak, J. V. *Nature* **1993**, *365*, 821.

(10) Cordes, A. W.; Haddon, R. C.; Oakley, R. T. *The Chemistry of Inorganic Ring Systems*; Steudel, R., Ed.; Elsevier: Amsterdam, 1992; Chapter 16.

(11) Bryan, C. D.; Cordes, A. W.; Goddard, J. D.; Haddon, R. C.; Hicks, R. G.; MacKinnon, C. D.; Mawhinney, R. C.; Oakley, R. T.; Palstra, T. T. M.; Perel, A. S. *J. Am. Chem. Soc.* **1996**, *118*, 330.

(12) (a) Hayes, P. J; Oakley, R. T; Cordes, A. W.; Pennington, W. T. *J. Am . Chem. Soc.* **1985**, *107*, 1346. (b) Cordes, A. W.; Koenig, H.; Oakley, R. T. *J. Chem. Soc., Chem. Commun.* **1989**, 710.

(13) Cordes, A. W.; Bestari, K. T.; Oakley, R. T. *J. Chem. Soc., Chem. Commun.* **1988**, 1328.

(14) A preliminary account of this work appeared in the Proceedings of the Seventh International Symposium on Inorganic Ring Systems: Chandrasekhar, V.; Vargas-Baca, I.; Chivers, T.; Ziegler, T. *Phosphorus, Sulfur Silicon* **1994**, *93*−94, 445.

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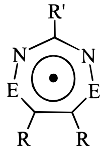
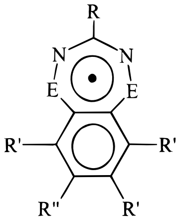
We have focused our attention on the seven-membered dithiadiazepinyl radicals (**4**). The electronic structure of the parent system **4a** was investigated by density functional theory (DFT) calculations. The potential for their use in conducting materials was estimated on the basis of the comparison of their dimerization and disproportionation energies with those of the dithiadiazolyl and dithiazolyl radicals. The theoretical study was extended to consider the selenium analog **4b**. The synthesis of the radicals **5a**−**c** was explored, and ESR spectroscopy was used to detect **5a** in solution. The N-silylated precursor **6c** was isolated and structurally characterized by X-ray crystallography.





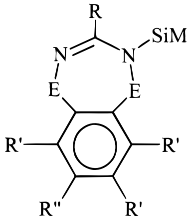
4a, E=S, R=R'=H

4b, E=Se, R=R'=H

5a, E=S, R=4-$CH_3C_6H_4$, R'=H, R"=CH_3

5b, E=S, R=Ph, R'=R"=H

5c, E=S, R=4-$CH_3C_6H_4$, R'= R"=Cl



6a, E=S, R=Ph, R'=H, R"=CH_3

6b, E=S, R=4-$CH_3C_6H_4$, R'= R"=H

6c, E=S, R=4-$CH_3C_6H_4$, R'=R"=Cl

Experimental Section

Reagents and General Procedures. Solvents were dried by treatment with the appropriate drying agent and freshly distilled before use. All reactions and the manipulation of moisture-sensitive products were carried out under an atmosphere of dry nitrogen by using Schlenk techniques or a Vacuum Atmospheres drybox.

The following commercial reagents were used as received: C_6H_4-1,2-$(SH)_2$ and 4-$CH_3C_6H_3$-1,2-$(SH)_2$, $(4\text{-}CH_3\ C_6H_4S)_2$, PhSeCl. Sulfuryl chloride, SO_2Cl_2, was distilled under N_2. Cl_2 was dried by passage through H_2SO_4. The trisilylated amidines $RCN_2(SiMe_3)_3$ (R = H, Ph, 4-$CH_3C_6H_4$) were prepared according to the published procedures.[15] The dithiol C_6Cl_4-5,6-$(SH)_2$ was prepared by a modification[16] of the original literature method[17] using an excess of iron. It was found that the preparation actually affords a mixture of C_6Cl_4-5,6-$(SH)_2$ and C_6Cl_5SH, the relative amounts of which were variable. Samples of C_6Cl_4-5,6-$(SH)_2$ purified by recrystallization from benzene and subsequent sublimation still contained small amounts of C_6Cl_5SH.

Instrumentation. ^1H and ^{13}C NMR spectra were run on Bruker ACE-200 and Bruker AM-400 spectrometers, respectively, operating at 200.132 and 76.132 MHz. Infrared spectra were recorded as Nujol mulls (KBr plates) on a Mattson 4030 FTIR spectrometer. EI mass spectra were measured on a Kratos MS80RFA instrument. ESR spectra were recorded by using a Bruker ER console and a Varian V3600 12-in. magnet equipped with a V/FR2503 Fieldial field controller. The microwave cavity was a Bruker Model 4102ST operating in the TE 102 mode. Microwave frequencies were measured with a Hewlett-Packard X532B absorption wave meter, and the magnetic field was determined with an Alpha Scientific 3093 digital NMR gaussmeter. Elemental analyses were performed within the Chemistry Department at the University of Calgary.

Reaction of 4-CH_3-1,2-$C_6H_3(SCl)_2$ with 4-$CH_3C_6H_4CN_2(SiMe_3)_3$ and PhSeCl. A solution of 4-$CH_3C_6H_3$-1,2-$(SH)_2$ (0.50 g, 3.2 mmol) in 150 mL of CH_2Cl_2 was treated with Cl_2 for 40 min at 0 °C. N_2 gas was bubbled through the solution for 20 min, and the solvent was evaporated to leave 4-CH_3-1,2-$C_6H_3(SCl)_2$ as an orange solid. A solution of 4-CH_3-1,2-$C_6H_3(SCl)_2$ in CH_2Cl_2 (200 mL) was added slowly (90 min) to a solution of 4-$CH_3C_6H_4CN_2(SiMe_3)_3$ (1.12 g, 3.2 mmol) in 200 mL of CH_2Cl_2 at −30 °C. After 18 h, a solution of PhSeCl (0.61 g, 3.2 mmol) in 50 mL of CH_2Cl_2 was added to the mixture. The reaction mixture changed color from orange to dark purple. After 2 h the solvent was evaporated and the dark residue was extracted repeatedly with hot hexanes (3 × 50 mL) to remove PhSeSePh leaving a dark brown residue (0.40 g). The ESR spectrum of this material gave a quintet in the ESR spectrum (see Results and Discussion). However, recrystallization attempts failed to purify the product.

Preparation of 4-$CH_3C_6H_4C(NSC_6Cl_5)(N(SiMe_3)_2)$ (9). A slurry of C_6Cl_5SH (1.68 g, 5.95 mmol) in CCl_4 was treated with dry Cl_2 during 40 min. The solvent was removed under vacuum, and the residue was redissolved in Et_2O (100 mL). This solution was slowly added to 4-$CH_3C_6H_4CN_2(SiMe_3)_3$ (6.0 mmol) in Et_2O. After the solution was stirred for 16 h, the solvent was evaporated and the solid residue recrystallized from Et_2O to give pale yellow crystals of **10** (yield 0.75 g, 24%). ^1H NMR ($CDCl_3$): δ 7.62, 7. 58, 7.14, 7.10 (A_2B_2 q, 4-$CH_3C_6H_4$, 4H), 2.34 (s, 4-$CH_3C_6H_4$, 3H), 0.26 (s, $Si(CH_3)_3$, 18H). IR (cm^{-1}, Nujol): 1453 s, 1375 m, 1335 m, 1252m, 919 m, 902 m, 878 w, 760 m, 692 m, 681 m, 665 m, 648 m, 483 s, 411 s. Mp: 151 °C. Anal. Calcd for $C_{20}H_{25}N_2SCl_5Si_2$: C, 42.98; H, 4.51; N, 5.01. Found: C, 43.16; H, 4.44; N, 4.99.

Reaction of C_6Cl_4-5,6-$(SCl)_2$ with 4-$CH_3C_6H_4CN_2(SiMe_3)_3$. A solution of C_6Cl_4-5,6-$(SH)_2$ (1.33 g, 4.7 mmol) in benzene was treated with Cl_2 for 25 min. The solvent was evaporated under vacuum to leave an orange residue. This was redissolved in Et_2O (60 mL) and decanted to remove a small amount of precipitated $(Cl_4C_6S_2)_2$, identified by EIMS. This solution was added dropwise to a solution of 4-$CH_3C_6H_4CN_2(SiMe_3)_3$ (1.65 g, 4.7 mmol) in 90 mL of Et_2O. After 2 days the solvent was evaporated to dryness leaving a foamy residue, which was rinsed with 10 mL of diethyl ether. Fractional recrystallization from diethyl ether afforded yellow prisms, which were identified as $\overline{S(C_6Cl_4)SN(SiMe_3)(4\text{-}CH_3C_6H_4)C{=}N}$ (**6c**) (0.528 g, 24%). ^1H NMR (ppm, $CDCl_3$): δ 7.47, 7.42, 7.20, 7.15 (A_2B_2 q, 4-$CH_3C_6H_4$, 4H), 2.38 (s, 4-$CH_3C_6H_4$, 3H), −0.02 (s, $Si(CH_3)_3$, 9H). IR (cm^{-1}, Nujol): 1332 m, 1317 m, 1304 m, 1286 m, 1254 m, 1172 m, 1105 m, 1091 m, 939 m, 835 s, 781 m, 636 m. Mp: 110 °C (dec). EIMS: *m/z* 482 (M^+), 292 ($Cl_4C_6S_2N^+$), 190 (4-$CH_3C_6H_4NSiMe_3^+$), 73 ($SiMe_3^+$). Anal. Calcd for $C_{17}H_{16}N_2S_2Cl_4Si$: C, 42.33; H, 3.34; N, 5.81. Found: C, 41.94; H, 3.22; N, 5.64. A second fraction was isolated and recrystallized twice from Et_2O to yield pale yellow flakes tentatively identified as $[C_6Cl_4SNC(4\text{-}CH_3C_6H_4)N(SiMe_3)S]_2{\cdot}Et_2O$. ^1H NMR (ppm, $CDCl_3$): δ 7.52, 7.48, 7.41, 7.37, 7.15, 7.11, 7.09, 7.05 (2 A_2B_2 q, 4-$CH_3C_6H_4$, 8H), 3.47 (q, $^3J(^1H-^1H)$ = 7 Hz, $(CH_3CH_2)_2O$, 4H), 2.35 (s, 4-$CH_3C_6H_4$, 3H), 2.31 (s, 4-$CH_3C_6H_4$, 3H), 1.20 (t, $^3J(^1H-^1H)$ = 7 Hz, $(CH_3CH_2)_2O$, 6H), 0.15 (s, $Si(CH_3)_3$, 18H). FABMS: *m/z* 686 {$Cl_4C_6[SNC(4\text{-}CH_3C_6H_4)NSiMe_3]_2$}. Anal. Calcd for $C_{34}H_{32}N_4S_4Cl_8Si_2{\cdot}C_4H_{10}O$: C, 43.94; H, 4.08; N, 5.39. Found: C, 43.74; H, 4.14; N, 5.28.

Reaction of 6c with SO_2Cl_2. A solution of **6c** (0.200 g, 0.4 mmol) in 10 mL of THF was frozen and allowed to melt slowly. When melting was complete, neat SO_2Cl_2 (0.059 g, 0.4 mmol) was added to this solution by syringe. After 40 min the mixture had a dark purple color which turned to a dark brown after 1 h. An excess of SO_2Cl_2 (1 mmol) was added. The mixture became red, and when it was left standing, small orange crystals were formed on the walls of the flask. After 14 h the solvent was removed under vacuum. It was observed that the

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[15] (a) Boeré, R. T.; Oakley, R. T.; Reed, R. W. *J. Organomet. Chem.* **1987**, *331*, 161. (b) Cordes, A. W.; Glarum, S. H.; Haddon, R. C.; Halford, R.; Hicks, R. G.; Kennepohl, D.K.; Oakley, R. T.; Palstra, T. T. M.; Scott, S. R. *J. Chem. Soc., Chem. Commun.* **1992**, 1265.

[16] Chivers, T.; Gamble, S. Unpublished results.

[17] (a) Baker-Hawkes, M. J.; Billing, E.; Gray, H. B. *J. Am. Chem. Soc.* **1966**, *88*, 21. (b) Wharton, E. J.; McCleverty, J. A. *J. Chem. Soc. A* **1969**, 2258.

Table 1. Crystallographic Data for **6c**

formula	$C_{17}H_{16}N_2S_2SiCl_4$	Z	4
fw	482.34	T (°C)	23
space group	$P2_1/a$	λ (Å)	0.710 69
a (Å)	12.585(3)	ρ_{calc} (g cm^{-3})	1.521
b (Å)	12.211(2)	μ (cm^{-1})	8.22
c (Å)	14.003(2)	R^a	0.042
β (deg)	101.86(2)	$R_w{}^b$	0.049
V (Å^3)	2106.0(7)	dimens (mm)	0.32 × 0.20 × 0.23

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w\Delta^2/\Sigma wF_o{}^2]^{1/2}$.

orange crystals decomposed to a dark brown powder even under a dry N_2 atmosphere. The ^1H NMR spectrum (CD_2Cl_2) of this material showed no signal other than that of the residual solvent. The EIMS displayed a pattern ($m/z = 292$) which can be attributed to $[Cl_4C_6S_2N]^+$.

X-ray Analysis. A pale yellow block-shaped crystal of **6c** was mounted on a glass fiber. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $30.0 < 2\theta < 50.0°$, corresponded to a primitive monoclinic cell. The data were corrected for Lorentz, polarization, and empirical absorption effects.[18] The structure was solved by direct methods[19] and expanded using Fourier techniques.[20] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the teXsan crystallographic software package.[21] Crystallographic data are given in Table 1.

Computational Details

All calculations were based on approximate density functional theory (DFT) within the local density approximation (LDA),[22] using the ADF program system developed by Baerends et al.[23,24] and vectorized by Raveneck.[25] The numerical integration was based on a scheme developed by te Velde.[26] All molecular dimensions were fully optimized, by a procedure based on the method developed by Versluis and Ziegler.[27] All bonding energies were evaluated by the generalized transition state method due to Ziegler and Rauk.[28] A double ζ Slater-type-orbital (STO) basis[29] was employed for the ns and np shells of the main group elements. This basis was augmented by a 3d STO function for sulfur and a 4d STO for selenium, and for hydrogen, a 2p STO was used as polarization. Electrons in lower shells were treated by the frozen core approximation.[57] A set of auxiliary[30] s, p, d, f, and g STO functions, centered on the different nuclei, was used in order to fit the molecular density and present Coulomb and exchange potentials accurately in each SCF cycle. Energy differences were calculated by the LDA energy expression due to Vosko et al.[31] with Becke's[32] exchange corrections and Perdew's nonlocal correlation correction.[33]

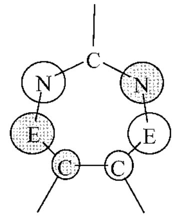

Figure 1. Calculated SOMO of the model ring $(HC)_2E_2N_2(CH)^{\bullet}$ (**4**; E = S, Se).

Results and Discussion

Electronic Structures of the Radicals $(HC)_2E_2N_2CH^{\bullet}$ (E = S, Se). The singly occupied molecular orbital for radicals of the type **4** is depicted in Figure 1. This orbital resembles the SOMO of the radical **3**;[1] it is N−E (E = S, Se) and C−C antibonding but bonding with respect to E−C. A nodal plane passes through the unique C atom.

Disproportionation Enthalpies. The energy of the process by which two neutral radicals ($N^{\bullet}$) generate the corresponding cation (C^+) and anion (A^-), $2N^{\bullet} \rightarrow C^+ + A^-$, is qualitatively identified with the electron−electron repulsion in the conduction band (ionic fluctuation energy) of a radical-stack material;[8] small interelectronic repulsions favor electrical conduction. In order to evaluate the potential application of cyclic radicals of the type $C_2S_2N_2C^{\bullet}$ for the construction of molecular conductors, it was considered of interest to calculate the disproportionation energy, and other related parameters, and to compare these values with those of the 1,2,3-dithiazolyl (**2**) and 1,2,3,5-dithiadiazolyl (**3**) radicals. To evaluate both the vertical ionization potential and electron affinity (ΔSCF), the optimized structure of the neutral heterocyclic radical was used in the calculation of the energy of the cation and the anion. The ionic structures were also optimized to calculate the corresponding adiabatic parameters. The disproportionation energy is calculated as the energy of the optimized anion and cation minus the energy of two neutral radical molecules. In addition, for a given ion, the energy difference between the optimized and nonoptimized structures is called the "relaxation energy"; it is a measure of the degree of structural reorganization upon electron transfer, and it should be small to facilitate electron conduction. Previously published theoretical studies on heterocycles of the types **3** are based on *ab initio* calculations. The results are sensitive to the inclusion of electron correlation and the order of perturbation which is employed.[34] The local density approximation (LDA) employed in our DFT calculations already considers electron correlation effects. In order to make a valid comparison, all the calculations were also carried out on models of **2** and **3**. The reliability of this study may be assessed by comparison of the calculated ionization potentials for the radicals **3** (E = S, 7.87 eV; E = Se, 7.70 eV) with the experimental values (E = S, 7.87 ± 0.03 eV; E = Se, 7.71 ± 0.03 eV).[34] Although there is excellent agreement between calculated and experimental values, the former data are employed mainly for a qualitative analysis. The results of all calculations are summarized in Table 2. Electron−electron repulsions were found to be smaller for the 7-membered than for the five-membered rings, as expected from the size of the rings. The

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(18) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351.

(19) SAPI91: Fan Hai-Fu. *Structure Analysis Programs with Intelligent Control*; Rigaku Corp.: Tokyo, 1991.

(20) DIRDIF92: Beuskens, P. T.; Admiraal, G.; Beuskens, G.; Bosman, W. P.; Garcia-Granda, R. S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *The DIRDIF program system, Technical Report of the Crystallography Laboratory*; University of Nijmegenm: Nijmegenm, The Netherlands, 1994.

(21) teXsan: *Crystal Structure Analysis Package*; Molecular Structure Corp., The Woodlands, TX, 1985, 1992.

(22) (a) Gunnarsson, O.; Lundquist, I. *Phys. Rev.* **1974**, *B10*, 1319. (b) Gunnarsson, O.; Lundquist, I. *Phys. Rev.* **1976**, *B13*, 4274. (c) Gunnarsson, O.; Johnson, M.; Lundquist, I. *Phys. Rev.* **1979**, *B20*, 3136.

(23) Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 41.

(24) Baerends, E. J. Ph.D. Thesis, Frije Universiteit, Amsterdam, 1975.

(25) Ravenek, W. *Algorithms and Applications on Vector and Parallel Computers*; Riele, H. J. J., Dekker, Th.J., van de Horst, H. A., Eds.; Elsevier: Amsterdam, 1987.

(26) te Velde, G. Ph.D. Thesis, Vrije Universiteit, Amsterdam, 1990.

(27) Versluis, L.; Ziegler, T. *J. Chem. Phys.* **1988**, *88*, 322.

(28) Ziegler, T.; Rauk, A. *Theor. Chim. Acta* **1977**, *46*, 1.

(29) (a) Snijders, J. G.; Baerends, E. J.; Vernoijs, P. *At. Nucl. Data Tables* **1982**, *26*, 483. (b) Vernoijs, P.; Snijders, J. G.; Baerends, E. J. *Slater Type Basis Functions for the Whole Periodic System, Internal Report*; Frije Universiteit: Amsterdam, 1981.

(30) Krijn, J.; Baerends, E. J. *Fitfunctions in the HFS Method, Internal Report*; Frije Universiteit: Amsterdam, 1984.

(31) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1990**, *58*, 1200.

(32) Becke, A. D. *J. Phys. Rev. A* **1988**, *38*, 2938.

(33) (a) Perdew, J. P. *Phys. Rev.* **1986**, *B33*, 8822. (b) Perdew, J. P. *Phys. Rev.* **1986**, *B34*, 7406.

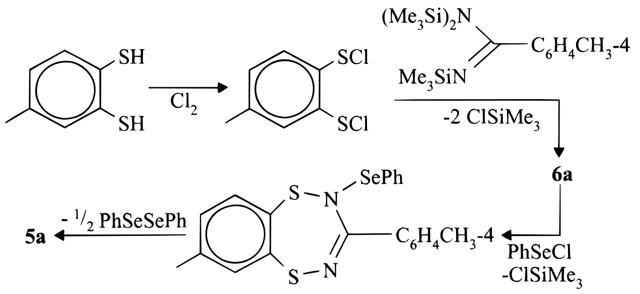
(34) Cordes, A. W.; Bryan, C. D.; Davis, W. M.; de Laat, R. H.; Glarum, S. H.; Goddard, J. D.; Haddon, R. C.; Hicks, R. G.; Kennepohl, D. K.; Oakley, R. T.; Scott, S. R.; Westwood, N. P. C. *J. Am. Chem. Soc.* **1993**, *115*, 7232.

Table 2. Comparison of Calculated Properties for Cyclic CSN and CSeN Radicals (in kJ mol^{-1})

	$(HC)_2S_2N$ (**2a**)	$(HC)_2Se_2N$ (**2b**)	$(HC)N_2S_2$ (**3a**)	$(HC)N_2Se_2$ (**3b**)	$(HC)_2N_2S_2(CH)$ (**4a**)	$(HC)_2N_2Se_2(CH)$ (**4b**)
vertical IP	670	664	759	743	851	827
vertical EA	6.09	33.0	106	132	280	285
adiabatic IP	664	663	756	743	797	737
adiabatic EA	24.1	50.2	132	157	291	296
relaxation enthalpy (+)[a]	−5.60	−1.29	−3.05	0.02	−53.6	−90.5
relaxation enthalpy (−)[b]	−18.0	−17.2	−26.0	−25.3	−10.9	−11.7
disprop enthalpy	640	613	623	585	506	440
dimerization energy	−12.5	−11.1	−21.7	−23.4	−14.1	−11.3

[a] For the corresponding cation. [b] For the corresponding anion.

Scheme 1



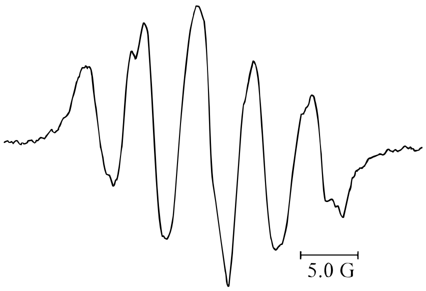


Figure 2. ESR spectra for the radical **5a**.

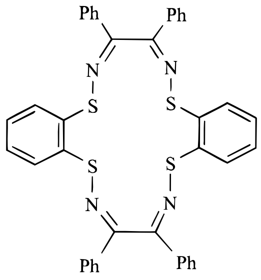
Se systems would offer smaller disproportionation energies than the analogous sulfur structures. On the other hand the "relaxation enthalpies" are considerably larger for the seven-membered ring cations.

Dimers: Structures and Dimerization Energies. The structure of the dimers of the radicals was optimized, assuming a face-to-face orientation, since this arrangement provides the best SOMO−SOMO overlap, although it is known that this may not be the arrangement observed in some solid structures.[35] The dimerization energy was calculated as the difference between the energies of two isolated radicals and that of the dimer. The results are given in Table 2.

The dimerization energy calculated for the dithiadiazolyl radicals **3** is of the same order of magnitude as the values obtained from MP3 calculations and experimental observations.[36] However, these dimerization energies are taken as a qualitative estimate of the dimerization tendency, since no zero point energy correction was applied. The calculations indicate that the dichalcogenadiazepinyl radicals have a smaller tendency to dimerization than the 1,2,3,5-dichalcogenadiazolyl radicals.

Synthetic Approaches to Dithiadiazepinyl Radicals. Reaction of 4-CH_3-1,2-$C_6H_3(SCl)_2$ with 4-$CH_3C_6H_4CN_2(SiMe_3)_3$ and PhSeCl. The preparation of the parent radicals **4a**,**b** would require the use of reagents of the type HE−C(R)=C(R)−EH (E = S, Se), which are not stable. A common approach for the preparation of related heterocycles is the use of a phenylene ring instead of the alkene. Our first attempt to synthesize the radical **5a** relied on the cyclocondensation of 4-methyl-benzene-1,2-bis(sulfenyl chloride) with a trisilylated benzamidine (see Scheme 1). The seven-membered ring precursor (**6a**), obtained in this way, has an N-bonded trimethylsilyl group which may be replaced by PhSe upon reaction with PhSeCl. Given the known tendency of the Se−N bond to undergo homolysis,[3] the PhSe-substituted derivative may decompose to the radical **5a**. The dark brown solid obtained in this manner displayed a quintet in the ESR spectrum (Figure 2), $g = 2.0070$ and $A_N(\text{iso}) = 4.9$ G. The hyperfine splitting is due to coupling with two ^{14}N atoms; the slight asymmetry is attributed to the methyl substituent on the phenylene ring. These ESR data are comparable to those of radicals which have similar SOMO compositions e.g. $RC(NSPh)_2^{\bullet}$ (**1**) (R = Ph, $g = 2.0071$, $A_N = 5.7$ G;[3] R = H, $g = 2.0070$, $A_N = 6.14$ G [4]) and $RCN_2S_2^{\bullet}$ (**3**) ($g \sim 2.01$, $A_N \sim 5$ G [1]). However, the attempted isolation of a pure sample of **5a** was frustrated by the presence of Ph_2Se_2 and, possibly, larger oligomers of **5a**, which have solubilities similar to that of **5a**. Sublimation attempts caused decomposition. The same difficulties were encountered when C_6H_4-1,2-$(SCl)_2$, and $PhCN_2(SiMe_3)_3$ were used to prepare **5b**.

Preparation of $\overline{S(C_6Cl_4)SN(SiMe_3)(4\text{-}CH_3C_6H_4C){=}N}$ (6c). The bifunctional nature of both starting materials (see Scheme 1) raises the possibility of polycyclocondensation reactions to form oligomers larger than a seven-membered ring in the first step of the synthesis. The related reaction of $C_6H_4(SCl)_2$ with $(PhC{=}NSiMe_3)_2$ affords the sixteen-membered ring $(H_4C_6)_2S_4N_4(CPh)_4$ (**7**) instead of an eight-membered heterocycle.[37] Consequently, we attempted to isolate and purify a precursor of the



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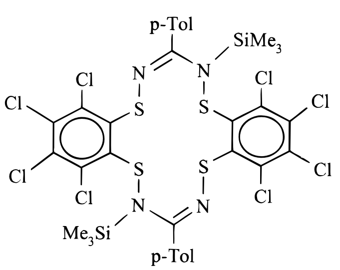

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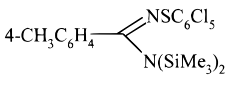

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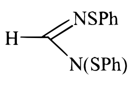

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(35) Awere, E. G.; Burford, N.; Haddon, R. C.; Parsons, S.; Passmore, J.; Waszczak, J. V.; White, P. S. *Inorg. Chem.* **1990**, *29*, 4821.

(36) Cordes, A. W.; Bryan, C. D.; Davis, W. M.; de Laat, R. H.; Glarum, S. H.; Goddard, J. D.; Haddon, R. C.; Hicks, R. G.; Kennepohl, D. K.; Oakley, R. T.; Scott, S. R.; Westwood, N. P. C. *J. Am. Chem. Soc.* **1993**, *115*, 7232.

(37) Sundermeyer, J.; Roesky, H. W.; Noltemeyer, M. *Can. J. Chem.* **1989**, *67*, 1785.

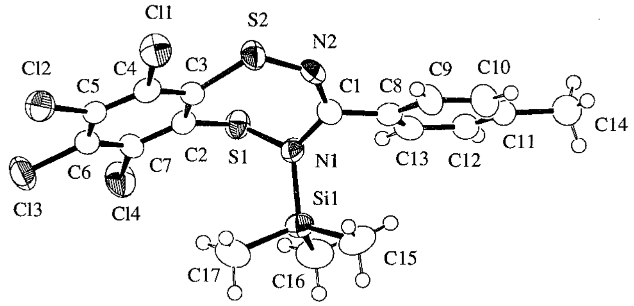

Figure 3. ORTEP diagram for **6c**.

type **6**, in order to simplify the purification of the target radical **5**. In the case of the reaction of 4-RC_6H_3-1,2-$(SCl)_2$ (R = H, Me) with 4-$CH_3C_6H_4CN_2(SiMe_3)_3$, the ^1H NMR of the products indicated that a very complex mixture had been obtained. Consequently, the dithiol C_6Cl_4-5,6-$(SH)_2$ was employed in the hope that its derivatives would be easier to isolate and purify. In the initial attempts the dithiol was chlorinated and used *in situ* for the reaction with 4-$CH_3C_6H_4CN_2(SiMe_3)_3$ in Et_2O. This method was successful in producing the precursor **6c**, as pale yellow crystals, in 24% yield. However, the ^1H NMR spectrum of the crude product of the reaction of C_6Cl_4-5,6-$(SCl)_2$ with 4-$CH_3C_6H_4CN_2(SiMe_3)_3$ displayed at least six signals of comparable intensities (δ 0.27, 0.26, 0.17, 0.15, 0.03, −0.02 ppm), in the region for $SiMe_3$ groups. The resonances for aromatic and methyl protons were also complicated but not as well resolved. The highest field $SiMe_3$ peak (δ −0.02 ppm) corresponds to **6c**. A second fraction was isolated and purified. It was shown to exhibit the resonance at $\delta = 0.15$ ppm. The rest of the spectrum for this product consisted of the signals of two different 4-$CH_3C_6H_4$ groups with equal integrations, as well as the resonances of Et_2O, persistent after two recrystallizations. The integrations suggest that there is one Et_2O molecule for two *p*-tolyl groups and two $SiMe_3$ groups. The elemental analysis for this material is consistent with the formula $C_{34}H_{32}N_4S_4Cl_8Si_2{\cdot}C_4H_{10}O$. The FABMS spectrum does not exhibit the molecular ion, but it does show an ion with *m*/*z* = 686, which was identified as $\{C_6Cl_4[SNC(4\text{-}CH_3C_6H_4)N(SiMe_3)]_2\}^+$ [i.e. $(M - C_6Cl_4S_2)^+$] on the basis of the isotopic distribution pattern. From these analytical data it is proposed that this second fraction is the 14-membered ring **8**. The four sulfur(II) centers in this heterocycle will produce a puckered structure (cf. **6c**); as a consequence the two *p*-tolyl resonances may arise from two conformers, e.g. chair and boat structures. We reiterate, however, that this product exhibits only one $SiMe_3$ resonance at $\delta = 0.15$ ppm. While **8** crystallizes from Et_2O as thin flakes, other solvents afford only amorphous powders, which has precluded structural characterization. The monosubstituted derivative 4-$CH_3C_6H_4C(N(SiMe_3)_2)(NSC_6Cl_5)$ (**9**) was isolated as a third impure fraction in small amounts. Its identity was corroborated by comparison of spectroscopic data with those of an authentic sample obtained by reaction of 4-$CH_3C_6H_4CN_2(SiMe_3)_3$ with C_6Cl_5SCl. The $SiMe_3$ resonance at δ 0.26 ppm was identified as due to this species. No other fractions could be purified. The formation of **9** results from the presence of C_6Cl_5SH as an impurity in C_6Cl_4-5,6-$(SH)_2$. The yield of **6c** is optimized when the reaction is carried out under high-dilution conditions keeping a 1:1 stoichiometry of reagents to minimize polycondensation. With this approach the product consisted mainly of **6c** and **9**.

Table 3. Bond Lengths (Å) and Bond Angles and Torsion Angles (deg) for **6c**

S(1)−N(1)	1.688(7)	S(1)−C(2)	1.763(8)
S(2)−N(2)	1.626(7)	S(2)−C(3)	1.774(8)
Si(1)−N(1)	1.800(7)	N(2)−C(1)	1.31(1)
N(1)−C(1)	1.40(1)	C(2)−C(3)	1.42(1)
N(1)−S(1)−C(2)	104.3(4)	N(2)−S(2)−C(3)	119.1(4)
S(1)−N(1)−Si(1)	117.3(4)	S(1)−N(1)−C(1)	117.9(6)
Si(1)−N(1)−C(1)	124.7(6)	S(2)−N(2)−C(1)	134.3(6)
N(1)−C(1)−N(2)	123.5(8)	S(1)−C(2)−C(3)	120.4(6)
S(2)−C(3)−C(2)	126.3(6)		
S(1)−N(1)−C(1)−N(2)	51.1(1)	C(1)−N(1)−S(1)−C(2)	−91.0(7)
S(1)−C(2)−C(3)−S(2)	1(1)	C(1)−N(2)−S(2)−C(3)	−5(1)
Si(1)−N(1)−C(1)−N(2)	−126.4(8)	S(2)−N(2)−C(1)−N(1)	6(1)
N(1)−S(1)−C(2)−C(3)	54.7(7)	Si(1)−N(1)−S(1)−C(2)	86.7(5)
N(2)−S(2)−C(3)−C(2)	−25.7(9)		

X-ray Structure of $S(C_6Cl_4)S(NSiMe_3)(4\text{-}CH_3C_6H_4C){=}N$ (6c). The heterocycle **6c** was structurally characterized by X-ray diffraction. An ORTEP diagram is shown in Figure 3. Relevant molecular dimensions are provided in Table 3. The puckered seven-membered ring displays localized single and double bonds. The −S−N< , −S−N=, and C−N bond distances, 1.688(7), 1.626(7), and 1.40(1) Å, respectively, are comparable to those observed for $HCN_2(SPh)_3$ (**10**).[4] The C=N distance, 1.31(1) Å, is slightly longer than the value of 1.261(5) Å found in that case. The N−C−N bond angle for **6c** is 123.5(8)°. The geometries at both C(1) and N(1) are planar (sum of bond angles ~ 360°). The N−C=N−S unit is also planar. These data indicate that there is no steric strain on the amidine moiety. The C−S distances of 1.763(8) and 1.774(8) Å are comparable to the average value of 1.763 Å observed for **7**.[37] The S−C−C bond angles for **6c** are 120.4(6) and 126.3(6)°; cf. values in the range 116−123.2° for **7**. The S−C−C−S torsion angles of **7** are 5.2 and 12.0°, while in **6c** the corresponding torsion angle is only 1°. The >N−S−C angle of 104.3° in **6c** is comparable to those observed for **7** and **10**, 99.5(4)−100.9(4) and 101.7(2)−103.1(2)°, respectively. Larger differences are apparent for S(2) and N(2): the =N−S−C and S−N=C bond angles, 119.1(4) and 134.3(6)°, are larger than those of **7** and **10**, 113.9(7)−117.8(7) and 119.6(3)°, respectively.

Reactions of $S(C_6Cl_4)S(NSiMe_3)(4\text{-}CH_3C_6H_4C){=}N$ (6c). In contrast to **6a**, the heterocycle **6c** was surprisingly unreactive toward PhSeCl and even toward 4-$CH_3C_6H_4SCl$. Consequently, the removal of the trimethylsilyl group by oxidation of **6c** with Cl_2 to give the corresponding cation was considered as an alternative route to the radical. The cation generated in this way could be reduced to the radical with Ph_3Sb; cf. the synthesis of **3**.[7] The reaction of **6c** with SO_2Cl_2 (or Cl_2 gas) was observed to occur in stages. Initially a dark purple species was generated followed by an orange crystalline material, which is stable only when an excess of Cl_2 is present in the reaction medium. When the Cl_2 was removed under vacuum a dark brown species was formed. These changes were reversed by adding Cl_2 to the reaction mixture. The process was monitored by ^1H NMR, and the spectrum displayed only the resonances of $ClSiMe_3$ and 4-$CH_3C_6H_4CN$. The EI-mass spectrum of the brown species showed $Cl_4C_6S_2N$ as the heaviest fragment (*m*/*z* = 292). It is tentatively proposed that Cl_2 oxidizes **6c** to the radical **5c**, which is then oxidized to the corresponding cation. Subsequently, a ring contraction to form *p*-tolunitrile and the 1,3,2-dithiazolium cation $C_6Cl_4S_2N^+$ (orange crystals) occurs (see Scheme 2). The dependence of the stability of these orange crystals on the presence of excess chlorine may be related to the formation of the Cl_3^- salt, which readily loses Cl_2 to give the Cl^- salt (the brown product). There are (at least) two precedents in the literature for the facile decomposition of Cl_3^- to Cl^- salts involving CSN cations.[38,39]

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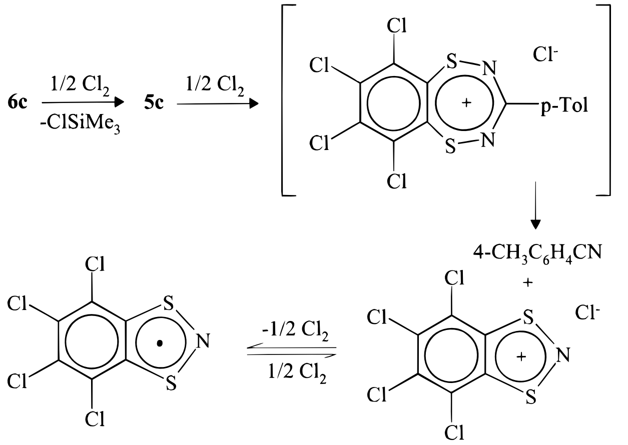
(38) Chivers, T.; Richardson, J. F.; Smith, N. R. M. *Inorg. Chem.* **1985**, *24*, 2453.

Scheme 2



Thermodynamics of the Ring Contraction. Main group heterocycles that are unstable with respect to ring contraction or expansion can sometimes be stabilized by high kinetic barriers. In the present case it is evident that no such barrier exists to prevent the decomposition of the seven-membered cation. The reaction enthalpy for this ring contraction was calculated from the total energies of the model rings 1,4,5,7-$(HC)_2S_2N_2(CH)$ (**4a**) and $(HC)_2S_2N$ (**2a**) and the elimination product HC≡N.

$$[(HC)_2S_2N_2(CH)]^+ \rightarrow [(HC)_2S_2N]^+ + HCN \quad \Delta H = -167.5 \text{ kJ mol}^{-1} \quad (1)$$

The calculations were repeated for the corresponding neutral radicals and anions.

$$[(HC)_2S_2N_2(CH)]^\bullet \rightarrow [(HC)_2S_2N]^\bullet + HCN \quad \Delta H = 3.6 \text{ kJ mol}^{-1} \quad (2)$$

$$[(HC)_2S_2N_2(CH)]^- \rightarrow [(HC)_2S_2N]^- + HCN \quad \Delta H = 234.2 \text{ kJ mol}^{-1} \quad (3)$$

Contraction of the cation with the elimination of HCN is a strongly exothermic process (eq 1). This can be understood by considering that the 8 π-electron antiaromatic ring fragments into a very stable 6 π-electron system and a strong C≡N bond. On the other hand the analogous process for the anion is strongly endothermic (eq 3). In this case a 10 π-electron aromatic system would generate an 8 π-electron antiaromatic ring. For the radicals it is predicted that the reaction would be approximately thermoneutral (eq 2), suggesting that such a radical would be stable only under mild conditions, consistent with our observations in the attempted purification of **5a**,**b**. In view of these calculations, the thermodynamically most favorable process to remove the $SiMe_3$ group from the precursor **6** would involve the formation of the corresponding anion. For a related example we note that the 10 π-electron 1,3,5,2,4-trithiadiazepine is formed by spontaneous HCl elimination from a saturated C−C precursor.[40]

Conclusions

DFT calculations have shown that 1,4,6,7-dichalcogenadiazepinyl radicals constitute an attractive possibility as building blocks for molecular conductors, because of their low disproportionation and dimerization energies. The existence of dithiadiazepinyl radicals of the type **5** was demonstrated by ESR spectroscopy. However, the isolation of a pure sample of these radicals was thwarted by their thermal instability. The silylated precursor $\overline{S(C_6Cl_4)SN(SiMe_3)(4\text{-}CH_3C_6H_4C)=N}$ was structurally characterized, but the neutral radical and the corresponding cation are thermally labile species. Further studies of this novel ring system should take into account the greater stability expected for the anionic species, which is a 10 π-electron system.

Acknowledgment. We thank the NSERC (Canada) for financial support, DGAPA-UNAM (Mexico) for a graduate scholarship (I.V.-B.), and Mr. Glen Bigam (University of Alberta) for recording the ESR spectra.

Supporting Information Available: Tables listing detailed crystallographic data, atomic positional and thermal parameters, and bond lengths and angles (15 pages). Ordering information is given on any current masthead page.

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(39) (a) Boeré, R. T.; Cordes, A. W.; Craig, S. L.; Oakley, R. T.; Reed, R. W. *J. Am. Chem. Soc.* **1987**, *109*, 868. (b) Chivers, T.; Richardson, J. F.; Smith, N. R. M. *Inorg. Chem.* **1986**, *25*, 47.

(40) Morris, J. L.; Rees, C. W. *J. Chem. Soc., Perkin Trans. 1* **1987**, 211.