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Novel photochemical ring contraction of 1,4,7,10-tetraisopropyldibenzo[*c,g*][1,2,5,6]tetrachalcogenocins: efficient synthesis, structure, and redox reactions of 1,4,6,9-tetraisopropylchalcogenanthrenes

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Abstract

1,4,7,10-Tetraisopropyldibenzo[*c,g*][1,2,5,6]tetrachalcogenocins, which were readily synthesized from 4,7-diisopropyl-2,2-dimethyl-1,3,2-benzodichalcogenastannoles, underwent selective ring contraction under irradiation with a high-pressure mercury lamp to give the corresponding 1,4,6,9-tetraisopropylchalcogenanthrenes in moderate yields. Facile one-electron redox reactions were observed between the chalcogenanthrenes and the corresponding stable chalcogenanthrenium radical cations by chemical or electrochemical treatment. © 1999 Elsevier Science Ltd. All rights reserved.

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The development of facile one-electron redox systems using an unusual π-electron framework is an attractive challenge. Recently, we reported the design of reversible one-electron redox systems using 4,7-disubstituted benzotrichalcogenoles and found by ESR spectroscopy that the radical cation salts obtained on treatment with one-electron oxidant have a 7π electron framework.[1] As a part of our search for new one-electron redox systems, we report here a very efficient and useful method for the synthesis of redox active chalcogenanthrenes with sterically hindering substituents on the benzene ring at adjacent positions of the 6-membered dichalcogenin unit. Although many chalcogenanthrene derivatives have been reported,[2] there are few chalcogenanthrenes containing carbon substituents on the benzene ring due to their synthetic limitation.[3] In the present work we report a novel synthetic route for the preparation of sulfur and/or selenium containing chalcogenanthrenes and the properties

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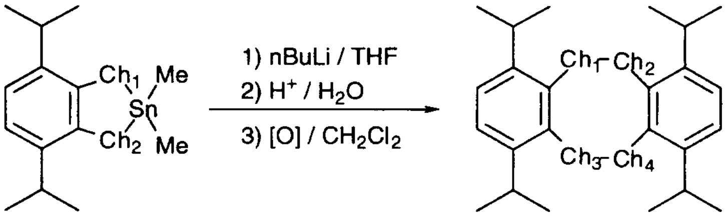
of the interconvertible redox structure bearing sterically hindered substituents on the benzene ring. Obviously, these chalcogenanthrene derivatives can serve as efficient precursors for novel one-electron redox systems.

4,7-Diisopropyl-2,2-dimethyl-1,3,2-benzodichalcogenastannoles (**1a**–**c**)[4] served as ideal starting materials for all preparative work. Reaction of stannoles with 2 equiv. of *n*-butyllithium, followed by acidification and air oxidation gave the corresponding tetrachalcogenocins (**2a**–**d**) as stable products which were purified by the usual work-up (Scheme 1). All physical and spectroscopic data supported the molecular structures of **2a**–**d**. The X-ray crystallographic analysis provided the most diagnostic information as to the cyclic constitution of **2a**. The molecular structure of **2a** is depicted in Fig. 1.[5] In addition to the tetrachalcogenocins mentioned above, there are some reports of X-ray analysis of tetrachalcogenocins and their dibenzo derivatives, namely, those that have chair conformation or twist conformation.[6] In our case, the 8-membered unit is in chair form, and the C–S–S–C torsional angle is 117.4(1)°.



1a : Ch$_1$,Ch$_2$ = S,S
1b : Ch$_1$,Ch$_2$ = Se,Se
1c : Ch$_1$,Ch$_2$ = S,Se

2a : Ch$_1$,Ch$_2$,Ch$_3$,Ch$_4$ = S,S,S,S 66%
2b : Ch$_1$,Ch$_2$,Ch$_3$,Ch$_4$ = Se,Se,Se,Se 60%
2c : Ch$_1$,Ch$_2$,Ch$_3$,Ch$_4$ = S,S,Se,Se 28% (69%†)
2d : Ch$_1$,Ch$_2$,Ch$_3$,Ch$_4$ = S,Se,Se,S 5% (16%†)

Scheme 1. †: Yield in the parenthesis was obtained by the following reaction conditions; (i) $SOCl_2$/THF, (ii) $LiAlH_4$/THF, (iii) H^+/H_2O, (iv) Et_3N–I_2/CH_2Cl_2

Irradiation of the benzene solution of tetrachalcogenocins (**2a**–**d**)[7] in a Pyrex vessel with a 100 W high-pressure mercury lamp under argon atmosphere gave the corresponding chalcogenanthrenes (**3a**–**c**) in moderate yields (Scheme 2, Table 1).[8] For instance, tetrathiocin (**2a**) was quantitatively converted to thianthrene (**3a**) in the photochemical reaction accompanied with the extrusion of two sulfur atoms. This ring contraction, however, did not occur thermally. It seems that these reactions proceeded via

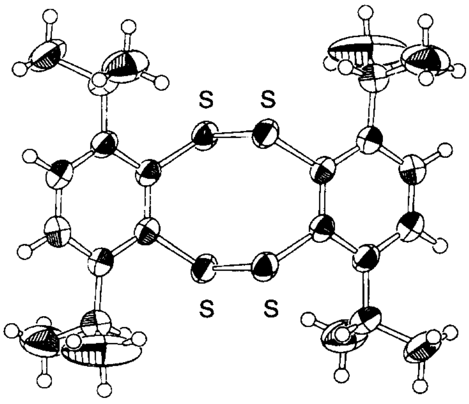
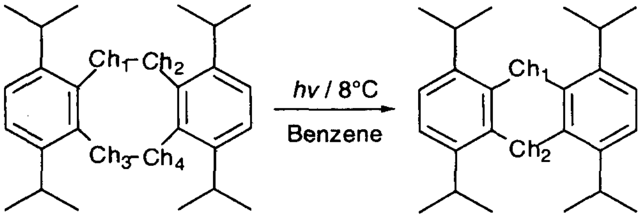


Figure 1. ORTEP drawing of **2a**

an excited singlet state because the reactions were not quenched under irradiation in the presence of some triplet quenchers such as oxygen. To explore the generality of the photochemical ring contraction, tetraselenocin (**2b**) and dithiadiselenocins (**2c**,**d**) were examined. Photolysis of tetraselenocin (**2b**) in benzene gave the desired 6-membered selenanthrene (**3b**) accompanied, however, with 5-membered triselenole (**4**). Furthermore, photolysis of two types of dithiadiselenocins (**2c**,**d**) in benzene gave two 6-membered thiaselenanthrene (**3c**) and thianthrene (**3a**) with 5-membered thiadiselenole (**5**) and 7-membered dithiaselenepin (**6**). The yields in Table 1 are those optimized after examination of the reaction conditions, and no further improvement was observed even with longer irradiation time (total 100 h). Further studies on the detailed mechanism of the photochemical ring contractions are in progress and will be discussed in a full paper. Although all physical and spectroscopic data supported the molecular structures of **3a**–**c**, one of the heterocyclic solid state structures, **3a**, was confirmed by X-ray crystallographic analysis (Fig. 2).[9] Thianthrene (**3a**) has a boat-form central ring, which is commonly referred to as a butterfly molecule with sterically hindering parts in both wings. The value of the folding angle (θ) of **3a** is 127.78, which is in good agreement with that of the parent thianthrene in the literature.[10]



2a : Ch1,Ch2,Ch3,Ch4 = S,S,S,S
2b : Ch1,Ch2,Ch3,Ch4 = Se,Se,Se,Se
2c : Ch1,Ch2,Ch3,Ch4 = S,S,Se,Se
2d : Ch1,Ch2,Ch3,Ch4 = S,Se,Se,S

3a : Ch1,Ch2 = S,S
3b : Ch1,Ch2 = Se,Se
3c : Ch1,Ch2 = S,Se

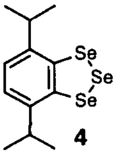
Scheme 2.

Analysis of the cyclic voltammetric responses is diagnostic for an essentially electrochemically reversible anodic step. Cyclic voltammograms of **3a**–**c** in acetonitrile at 20°C under argon atmosphere exhibited a quasi-reversible redox wave (**3a**: E_{pa}=0.94, E_{pc}=0.85) and irreversible waves (**3b**: E_{pa}=0.90; **3c**: E_{pa}=0.94) versus Ag/0.01 mol dm^{-3} AgNO$_3$.[11] It is a well-known fact that increasing selenium substitution normally leads to the lowering of the oxidation potential of a donor. As expected, with

Table 1
Photolysis of **2a**–**d**

Substrate	Time(h)	Yield (%)
2a	6	98 (**3a**)
2b	50	54 (**3b**)‡
2c	48	14 (**3c**)§
2d	48	11 (**3c**)¶

‡ : **4** (31%)
§ : **3a** (21%), **5** (10%), **6** (19%)
¶ : **3a** (19%), **5** (7%), **6** (19%)



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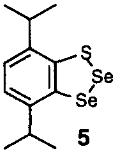

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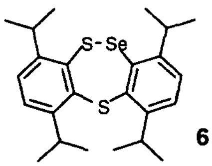

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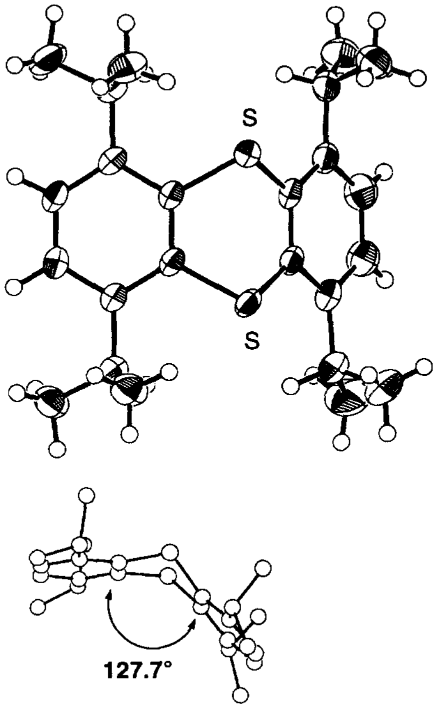
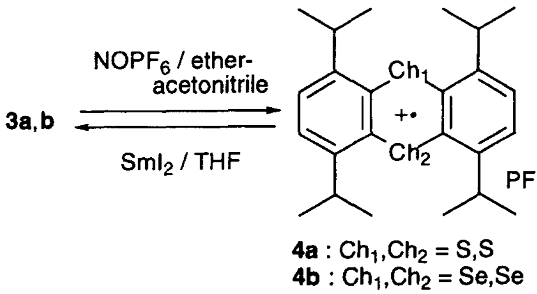


Figure 2. ORTEP drawing of **3a**

increasing selenium substitution, lowered oxidation peaks and less reversible sweeps were obtained which could be explained by assuming a higher degree of localization of electron deficiency to the selenium rather than the sulfur. This reflects a higher reactivity of the corresponding radical cation containing a selenium atom.

The corresponding radical cation salts (**4a**,**b**) were isolated in one-electron oxidation of **3a**,**b** with 1 equiv. of $NOPF_6$ in ether–acetonitrile quantitatively (Scheme 3). The dark purple salts (**4a**,**b**) were stable and the structure was determined by physical and spectroscopic analysis.[12,13] The ESR spectra of **4a**,**b** in acetonitrile showed the presence of peaks (**2a**: g=2.0071, a_{H1}=0.124, a_{H2}=0.013, Fig. 3; **2b**: g=2.0241, broad peak) attributable to a radical character. The salts (**4a**,**b**) underwent one-electron reduction by treatment with 1 equiv. of samarium(II) iodide in THF to give **3a**,**b** quantitatively.



Scheme 3.

We have succeeded in preparing chalcogenanthrenes with sterically hindering substituents by novel photochemical ring contraction of tetrachalcogenocins. These functionally substituted stable compounds should be useful material for construction of a new reversible one-electron redox system.

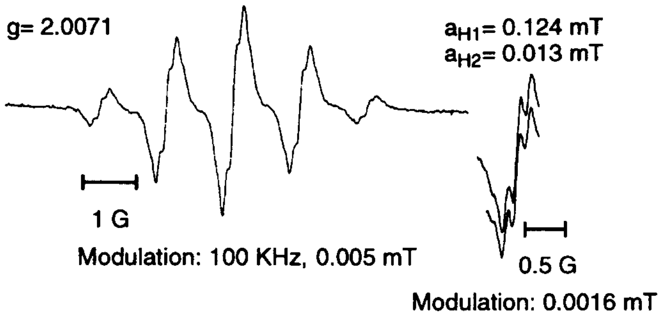


Figure 3. ESR spectra of **4a**

Acknowledgements

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References

1. Ogawa, S.; Kikuchi, T.; Niizuma, S.; Sato, R. *J. Chem. Soc., Chem. Commun.* **1994**, 1593–1594; Ogawa, S.; Saito, S.; Kikuchi, T.; Kawai, Y.; Niizuma, S.; Sato, R. *Chem. Lett.* **1995**, 321–322; Ogawa, S.; Nobuta, S.; Nakayama, R.; Kawai, Y.; Niizuma, S.; Sato, R. *ibid.* **1996**, 757–758; Ogawa, S.; Ohmiya, T.; Kikuchi, T.; Kawai, Y.; Niizuma, S.; Sato, R. *Heterocycles* **1996**, *43*, 1843–1846; Schröder, D.; Schwarz, H.; Löbrecht, B.; Koch, W.; Ogawa, S. *Eur. J. Inorg. Chem.* **1998**, 983–987.
2. Dougherty, G.; Hammond, P. D. *J. Am. Chem. Soc.* **1935**, *57*, 117–118; Nakanishi, W.; Ikeda, Y. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1651–1664; Nakayama, J.; Kashiwagi, M.; Yomoda, R.; Hoshino, M. *Nippon Kagaku Kaishi* **1987**, 1424–1429; Engman, L.; Hellberg, J.; Ishag, C.; Söderholm, S. *J. Chem. Soc., Perkin Trans. 1* **1988**, 2095–2101; Furukawa, N.; Kimura, T.; Horie, Y.; Ogawa, S. *Heterocycles* **1991**, *32*, 675–678; Dötze, M.; Klar, G. *Phosphorus, Sulfur Silicon Relat. Elem.* **1993**, *84*, 95–106; Engman, L.; Eriksson, P. *Heterocycles* **1996**, *43*, 861–871.
3. Lovell, J. M.; Joule, J. A. *J. Chem. Soc., Perkin Trans. 1* **1996**, 2391–2395; Lovell, J. M.; Beddoes, R. L.; Joule, J. A. *Tetrahedron* **1996**, *52*, 4745–4756.
4. Ogawa, S.; Kikuchi, T.; Sasaki, A.; Chida, S.; Sato, R. *Tetrahedron Lett.* **1994**, *35*, 5469–5472.
5. X-Ray diffraction data for **2a**: $C_{24}H_{32}S_4$, monoclinic, space group $P2_1/n$(#14), a=11.471(1) Å, b=5.958(1) Å, c=18.039(1) Å, β=102.284(8)°, V=1204.6(3) Å^3, Z=2, D_{calc}=1.237 g cm^{-3}. The intensity data were collected on a Rigaku AFC7R diffractometer with filtered Cu-Kα radiation at 295 K. Of the 2552 reflections which were collected, 2424 were unique. The structure was solved by direct method (SHELXS86) and expanded using Fourier techniques (DIRDIF94). The final cycle of full-matrix least-squares refinement was based on 2046 observed reflections ($I > 1.00\ \sigma(I)$) and 144 variable parameters with R=0.046, R_w=0.081. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (CCDC).
6. Setzer, W. N.; Glass, R. S. In *Conformational Analysis of Medium-Sized Heterocycles*; Glass, R. S., Ed. Conformational analysis of medium-sized sulfur-containing heterocycles. VCH Publishers: New York, 1988; pp. 151–180. For recent examples, see: Lakshmikantham, M. V.; Raasch, M. S.; Cava, M. P.; Bott, S. G.; Atwood, J. L. *J. Org. Chem.* **1987**, *52*, 1874–1877; Yang, X.; Rauchfuss, T. B.; Wilson, S. *J. Chem. Soc., Chem. Commun.* **1990**, 34–36; Borisenko, K. B.; Broschag, M.; Hargittai, I.; Klapötke, T. M.; Schröder, D.; Schulz, A.; Schwarz, H.; Tornieporth-Oetting, I. C.; White, P. S. *J. Chem. Soc., Dalton Trans.* **1994**, 2705–2712; Shimizu, T.; Iwata, K.; Kamigata, N. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2357–2359.
7. UV-spectra of **2a–d**: **2a**, λ_{max} ($CHCl_3$)/nm 316 (ε/dm^{-3} mol^{-1} cm^{-1} 4800); **2b**, 263 (13400) and 322 (4600); **2c**, 317 (3700); **2d**, 255 (26700) and 319 (7500).
8. Very recently, similar photochemical reactions of tetrathiocins have been reported, see: Chivers, T.; Parvez, M.; Vargas-Baca, I.; Schatte, G. *Can. J. Chem.* **1998**, *76*, 1092–1101.

9. X-Ray diffraction data for **3a**: $C_{24}H_{32}S_2$, monoclinic, space group $P2_1/n$(#14), a=11.050(2) Å, b=16.593(2) Å, c=11.936(2) Å, β=91.95(1)°, V=2187.2(4) Å^3, Z=4, D_{calc}=1.168 g cm^{-3}. The intensity data were collected on a Rigaku AFC7R diffractometer with filtered Cu-Kα radiation at 295 K. Of the 5520 reflections which were collected, 4192 were unique. The structure was solved by direct method (SIR92) and expanded using Fourier techniques (DIRDIF94). The final cycle of full-matrix least-squares refinement was based on 3478 observed reflections ($I > 1.50\ \sigma(I)$) and 364 variable parameters with R=0.053, R_w=0.069. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (CCDC).
10. Hargittai, I.; Rozsondai, B. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S.; Rappoport, Z., Eds. Structural chemistry of organic compounds containing selenium or tellurium. John Wiley and Sons: New York, 1986; Vol. 1, pp. 63–155.
11. Cyclic voltammograms of **3a–c** (2.0 mmol dm^{-3}) were measured in acetonitrile at 20°C containing 0.1 mol dm^{-3} Bu_4NClO_4 as a supporting electrolyte using a glassy-carbon working electrode and Ag/0.01 mol dm^{-3} $AgNO_3$ couple in acetonitrile as a reference electrode; scan rate 100 mV s^{-1}.
12. Murata, Y.; Shine, H. J. *J. Org. Chem.* **1969**, *34*, 3368–3372; Bandlish, B. K.; Shine, H. J. *ibid.* **1977**, *42*, 561–563; Boduszek, B.; Shine, H. J. *ibid.* **1988**, *53*, 5142–5143; Bock, H.; Pittmeyer, P. *Phosphorous, Sulfur Silicon Relat. Elem.* **1992**, *68*, 261–291; Bock, H.; Rauschenbach, A.; Näther, C.; Kleine, M.; Havlas, Z. *Chem. Ber.* **1994**, *127*, 2043–2049; Zhao, W.; Shine, H. J.; Whittlesey, B. R. *J. Org. Chem.* **1997**, *62*, 8693–8701; Doménech, A.; Casades, I.; Garía, H. *ibid.* **1999**, *64*, 3731–3735.
13. **4a**: Dark purple powder (The color has been unchanged in water for 10–20 min); mp 164.5–165.0°C (decomp.); ^{31}P NMR (162 MHz, CD_3CN, 298K) δ −143.7 (sept, J_{PF}=706 Hz); Anal. calcd for $C_{24}H_{32}S_2PF_6$: C, 54.43, H, 6.09. Found: C, 54.54, H, 6.06%. **4b**: Dark purple powder; mp 78.5–79.0°C (decomp.); ^{31}P NMR (162 MHz, CD_3CN, 243K) δ −143.8 (sept, J_{PF}=707 Hz); Anal. calcd for $C_{24}H_{32}Se_2PF_6$: C, 46.24, H, 5.17. Found: C, 45.88, H, 5.37%. We have so far been unable to obtain radical cation salt (**4c**) from thiaselenanthrene (**3c**) suitable for elemental analysis due to its inherent instability.