Radialenes

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Planar [6]Radialenes: Structure, Synthesis, and Aromaticity of Benzotriselenophene and Benzotrithiophene**

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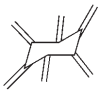
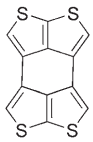
Radialenes (e.g. [6]radialene, **1**) are a relatively modern class of alicyclic hydrocarbons in which all carbon atoms in the ring are sp^2 hybridized and there are as many exocyclic double bonds as possible.[1,2] The first radialene, 7,8,9,10,11,12-hexamethyl[6]radialene, was prepared by Hopff and Wick in 1961.[3] Radialenes and their derivatives have been the subject of significant theoretical and experimental interest.[1,2,4,5] New approaches to the synthesis of radialenes have been developed, and these structures have become important building blocks for organic conductors and ferromagnets.[1,2,6] Radialenes are also of considerable interest because of their exocyclic double bonds, aromaticity, and conjugation.[1,2,4a] The parent [3]-, [4]-, [5]-, and [6]radialenes polymerize at room temperature and are unstable in air; however, many stable derivatives are known.[1,2] It has been found experimentally that [3]-[7] and [4]radialenes[8] usually have a planar structure.[9] [5]Radialenes, such as decamethyl[5]radialene, usually have a twisted-envelope or half-chair conformation.[10] In contrast to [3]-, [4]-, and [5]radialenes, [6]radialenes (of type **1**) have a chair conformation, according to both experimental and theoretical studies.[1,2,11] Perylene and triphenylene may not be considered as radialenes, because the π electrons are delocalized over an aromatic sextet.[2] On the other hand, the condensed-thiophene-fused compounds **2**[12] and **3**,[13] which are isoelectronic with perylene, belong to the [6]radialene family.[2] To the best of our knowledge, the only known example of a planar [6]radialene is compound **2**.[12]



1

Herein, we report the efficient synthesis, X-ray crystal structures, and characterization of previously unknown benzo[1,2-c:3,4-c′:5,6-c″]triselenophene (**5**) and its known[14] sulfur analogue, benzo[1,2-c:3,4-c′:5,6-c″]trithiophene (**4**). Two other important compounds, the previously unknown selenophene-fused [8]annulene **7** and its known sulfur analogue **6**[15] were also synthesized as side products.[16] Both **4** and **5** are rare examples of planar [6]radialenes. They display an unusual geometry, electronic structure, and lack of aromaticity in the planar six-membered ring.



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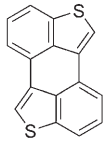
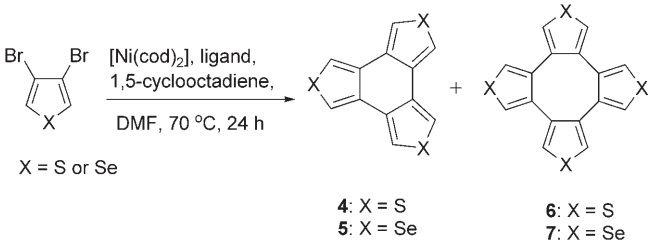


3

We prepared compound **4** in one step from commercially available 3,4-dibromothiophene (Scheme 1).[17] The coupling of 3,4-dibromothiophene with $[Ni(cod)_2]$ in the presence of 1,5-cyclooctadiene (cod) and the neutral ligand Ph_3P in dry acetonitrile produced compounds **4** and **6** in a 1:1 ratio



Scheme 1. Preparation of compounds **4**–**7** by nickel-catalyzed cyclooligomerization. DMF = *N*,*N*-dimethylformamide.

(Table 1).[17,18] Compounds **4** and **6** are white solids that are moderately soluble in organic solvents, such as hexane, $CHCl_3$, and dichloromethane. The same products were obtained, but in a different ratio, when 2,2′-bipyridyl was used as the neutral ligand (Table 1). To prepare **5** and **7** (the previously unknown selenium analogues of **4** and **6**, respectively), 3,4-dibromoselenophene[19] was treated similarly with

Table 1: Yields of **4**–**7** from the reaction in Scheme 1.

X	Ligand	Yield of **4** (X = S) or **5** (X = Se) [%][a]	Yield of **6** (X = S) or **7** (X = Se) [%][a]
S	Ph_3P	40	40
S	2,2′-bipyridyl	14	60
Se	Ph_3P	50	10
Se	2,2′-bipyridyl	30	5

[a] Yield of the isolated product.

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Supporting information for this article (including experimental and computational details, spectral data, CV data for compounds **4**–**7**, and pictures of the crystal packing of **4** and **5**) is available on the WWW under http://www.angewandte.org or from the author.

$[Ni(cod)_2]$ in the presence of 1,5-cyclooctadiene and a neutral ligand (Ph_3P or 2,2′-bipyridyl) in dry acetonitrile (Table 1).[17] Unlike the sulfur analogues **4** and **6**, the selenium compounds **5** and **7** are poorly soluble in common organic solvents.

Single crystals of **4** and **5** were grown by slow evaporation of solutions of the compounds in chloroform at room temperature. X-ray crystal structures of **4** and **5** are shown in Figure 1, and structural data, both experimental and calculated (at the B3LYP/6-31G(d) level), are given in Table 2. The calculated bond lengths are very close to the experimental values (within 0.01 Å); our discussion is based on the experimental values, unless stated otherwise. Both **4** and **5** are practically planar: The average dihedral angle in the central six-membered ring is only 2.2° for compound **4**[20] and 3.0° for compound **5**.[21] The calculated[17] optimized structures

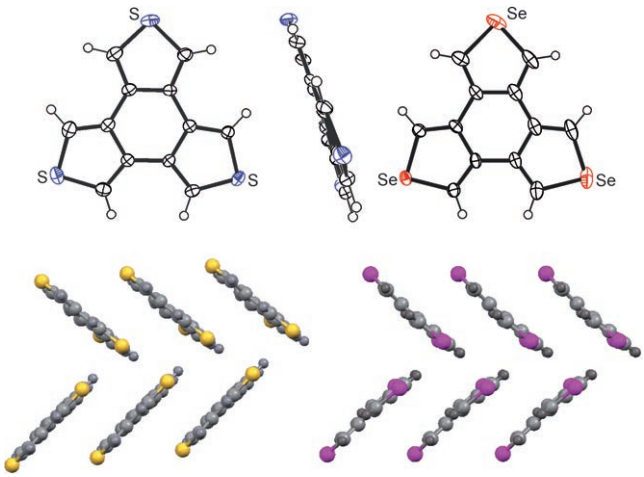

Figure 1. X-ray crystal structures (top: ORTEP diagrams; bottom: packing pattern) of compounds **4** (left; two molecules are shown in the ORTEP diagram)[20] and **5** (right). See Table 2 for bond lengths and bond angles. In both structures, stacking molecules are positioned on the same translation axis (*b* axis for **4** and *c* axis for **5**).

Table 2: Measured and calculated[a] bond lengths and bond angles for **4** and **5**. (The values for compound **2** are given for comparison.)

	Bond lengths [Å]			Bond angles [°]	
	endo[b]	*exo*[b]	exocyclic C=C[b]	*endo*[c]	*exo*[c]
4[d]	1.439	1.463	1.371	112.0	128.0
	(1.449)	(1.462)	(1.373)	(112.1)	(127.9)
5[d]	1.451	1.463	1.363	114.3	125.7
	(1.453)	(1.466)	(1.370)	(114.0)	(126.0)
2[e]	1.440	1.452	1.368	112.3	135.4
	(1.438)	(1.466)	(1.372)[f]	(112.7)[f]	(134.7)

[a] The bond lengths and bond angles calculated at the B3LYP/6-31G(d) level are given in parenthesis. [b] An *endo* bond is a bond shared by the six-membered ring and a five-membered ring, whereas an *exo* bond connects two heterocyclic rings. An exocyclic C=C bond[23] is a bond exocyclic to the six-membered ring. [c] An *endo* bond angle is a C-C-C angle inside a heterocyclic ring, whereas the *exo* bond angles are the angles outside the heterocyclic and central rings. [d] Average measured values for three bonds or three bond angles are given. Measured values are within 0.01 Å or 1° of the average value. [e] Average measured values from reference [12a]. [f] Average values for two different *endo* bonds or bond angles.

of **4** and **5** are planar with D_{3h} symmetry, as confirmed by frequency analysis. Surprisingly, the bonds in the central six-membered ring of both **4** and **5** are unusually long for aromatic C–C bonds, with an average length of 1.451 Å in **4** and 1.457 Å in **5**.[22] The C–C bonds in benzene are significantly shorter at 1.40 Å in length. The exocyclic double bonds[23] in **4** and **5** are relatively short, with lengths of 1.371 and 1.363 Å, respectively. The lengths of all bonds exocyclic to the six-membered ring fall within the range of C–C bond lengths for double bonds. Thus, it is clear that **4** and **5** are members of the radialene family. Interestingly, in contrast to their parent analogues, the [6]radialenes **4** and **5** have planar backbones.

The X-ray crystal structures of both **4** and **5** show that the molecules are well organized for good electron transport (Figure 1). Two types of packing are observed: π–π stacking and a herringbone pattern (Figure 1, bottom). The distances between π–π-stacked molecules in **4** and **5** are 3.39 (average) and 3.48 Å, respectively, and are thus similar to the equilibrium van der Waals distance of 3.4 Å between two sp^2-hybridized carbon atoms. For comparison, the interplanar distance between tetracene units in rubrene (record high mobility has been demonstrated for rubrene in organic field-effect transistors)[24a] is about 3.7 Å.[24] The C···C distances between the two molecules packed in herringbone fashion are also short: 3.3 and 3.4 Å in crystals of **4** and 3.5 Å in crystals of **5**. The angles between the two molecules packed in herringbone fashion are 73.3 and 85.4° for radialene **4** and 63.8 and 83.2° for radialene **5**. The corresponding angles are 53° in pentacene,[24a] approximately 62° in rubrene,[24b,c] and 53[25a] and 63°[25b] in α-sexithienyl.

The calculated values of the nucleus-independent chemical shifts (NICS)[26] are close to zero for the central ring in compounds **4** and **5** (Table 3).[27] Consequently, on the basis of NICS criteria, this ring can be considered to be practically non-aromatic. The long C–C bonds in the central ring of compounds **4** and **5** also indicate a lack of aromaticity.[28]

Table 3: NICS(0) and NICS(1) values[26] calculated at the B3LYP/6-31G(d)//B3LYP/6-31G(d) level for the central and heterocyclic rings of compounds **2**, **4**, and **5**.

	Central ring		Heterocyclic rings	
	NICS(0) [ppm]	NICS(1) [ppm]	NICS(0) [ppm]	NICS(1) [ppm]
4	1.9	−1.6	−12.2	−9.6
5	2.6	−1.2	−11.6	−9.3
2	3.7	0.2	−10.1	−7.7

Interestingly, the $C(sp^2)$–$C(sp^2)$ bond length calculated for benzene in the pure sigma state is 1.45 Å,[29] which is very close to the C–C bond length found for the central ring of **4** and **5**. A pure sigma state does not include any contribution from π orbitals and is therefore absolutely non-aromatic. A lack of aromaticity combined with the planarity of compounds **4** and **5** is surprising, as all carbon atoms are sp^2 hybridized. According to the NICS criteria, the heterocyclic rings in compounds **4** and **5** maintain their aromaticity (Table 3).[30]

The *endo* bond angles in the thiophene and selenophene rings of **4** and **5** are 112.0 and 114.3°, respectively, and thus significantly smaller than the 120° required for ideal planar [6]radialene. Therefore, a positive strain-induced bond localization (SIBL) or Mills–Nixon effect[31] can be expected; that is, the presence of long *endo* C–C bonds and short *exo* C–C bonds. However, radialenes **4** and **5** show negative SIBL with *endo* C–C bonds that are slightly shorter than *exo* C–C bonds (Table 2). The aromaticity of the heterocyclic rings forces the *endo* C–C bonds to become shorter than the $C(sp^2)$–$C(sp^2)$ bonds, which usually have a length of 1.49 Å[2,32] in [6]radialenes.[22,33] As a result of the SIBL effect, the *exo* C–C bond is shortened relative to the usual $C(sp^2)$–$C(sp^2)$ bond length.[34]

The UV spectra of compounds **4**–**7** show strong absorption peaks at around 250–270 nm (Figure 2), which correspond to absorption by thiophene and selenophene units.[35] The strongest absorption peak observed for compound **4** (at 254 nm) is blue shifted by 23 nm (0.49 eV) relative to the absorption of the parent thiophene (231 nm). A similar blue shift of 17 nm (0.32 eV) was observed for compound **5** (266 nm) relative to the parent selenophene (249 nm). These blue shifts result mostly from conjugation between heterocyclic rings in compounds **4** and **5**.[36]

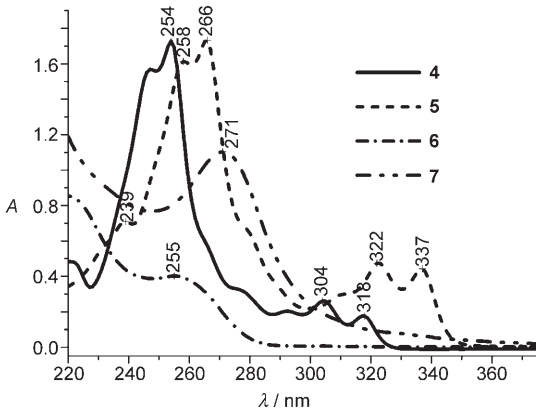

Figure 2. UV/Vis absorption spectra of compounds **4**–**7**.

Compound **4** has additional absorption peaks at 292–318 nm, which apparently originate from interactions between the heterocyclic rings through the central ring. In compound **5**, these absorptions are blue shifted to 307–337 nm. These absorption bands are absent in the spectra of compounds **6** and **7**, probably owing to a lack of conjugation between heterocyclic units through the central ring. The calculated (TD-B3LYP/6-31G(d)) absorption peak for compound **4** for the longest-wavelength transition is at 300 nm and includes degenerate HOMO–LUMO and HOMO−1–LUMO transitions.[37] This peak is absent in UV spectra of the parent fragments, namely thiophene and selenophene molecules. A frontier-orbital picture provides more insight into the origin of the new absorption peak at around 320 nm for compounds **4** and **5** (Figure 3). The HOMO−1 and HOMO are degenerate. They can be considered as antibonding combinations of the HOMO−1 and HOMO of thiophene and thus result in antibonding orbital combinations at the central six-membered ring.[38,39] In contrast, the LUMO can be considered as a bonding combination of the LUMOs of thiophene units. This interaction results in a bonding orbital combination at the central six-membered ring (Figure 3).[40]

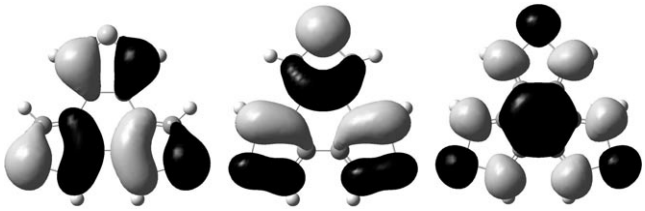

Figure 3. HOMO−1 (left), HOMO (middle), and LUMO (right) of compound **4** (at the B3LYP/6-31G(d) level).

We studied the redox behavior of compounds **4**–**7** by cyclic voltammetry (CV, see Figure S3 in the Supporting Information).[17] No reduction peak was observed at potentials of up to −2 V. All oxidation peaks are irreversible, which might indicate the oligomerization of these molecules under CV conditions. Radialenes **4** and **5** were oxidized at lower potentials than the corresponding higher cyclooligomers **6** and **7** by about 0.2 V.[41]

In conclusion, we have studied a new family of planar non-aromatic [6]radialenes both experimentally and theoretically and developed a simple method for the synthesis of [6]radialenes containing thiophene and selenophene units. X-ray crystal-structure analysis showed unexpectedly that the [6]radialenes **4** and **5** are completely planar. According to both experimental and theoretical results, the average C–C bond length in the six-membered rings of **4** and **5** is unusually long, at around 1.44–1.46 Å. Despite their planarity and the sp^2 hybridization of all carbon atoms, the central six-membered rings in **4** and **5** are non-aromatic. Compounds **4** and **5** have an unusual electronic structure and solid-state packing, which involves a combination of π–π stacking and a herringbone pattern. Therefore, important applications as organic electronic materials are expected. We are currently investigating the application of compounds **4** and **5** in organic field-effect transistors.

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[20] The unit cell of compound **4** consists of two very similar independent molecules. Average values for these two molecules are used in the discussion.

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[27] For comparison, the NICS(0) and NICS(1) values calculated for benzene at the B3LYP/6-31G(d)//B3LYP/6-31G(d) level are $\delta = -9.7$ and -11.2 ppm, respectively.

[28] Furthermore, comparison of the X-ray structure of compound **4** with that of compound **6**[15] revealed that the bond lengths in the central ring are similar for the two compounds. Thus, the lengths of the *exo* C–C bonds are 1.469 Å in **6** and 1.463 Å in **4**, and the lengths of the *endo* C–C bonds are 1.436 Å in **6** and 1.439 Å in **4**. As aromaticity and antiaromaticity effects are irrelevant with respect to the central ring in **6**, which is not planar, the central ring in compound **4** must also be non-aromatic, in accordance with the NICS results.

[29] P. C. Hiberty, D. Danovich, A. Shurki, S. Shaik, *J. Am. Chem. Soc.* **1995**, *117*, 7760 – 7768; therein, the pure sigma state is called a quasiclassical state.

[30] The NICS(0) and NICS(1) values calculated at the B3LYP/6-31G(d)//B3LYP/6-31G(d) level for the parent thiophene ($\delta = -13.5$ and -10.5 ppm, respectively) are only slightly more negative than those for the thiophene rings in compound **4**. The calculated NICS(0) and NICS(1) values for the parent selenophene are $\delta = -14.5$ and -10.8 ppm, respectively.

[31] a) A. Stanger, *J. Am. Chem. Soc.* **1991**, *113*, 8277 – 8280; b) A. Stanger, *J. Am. Chem. Soc.* **1998**, *120*, 12034 – 12040; c) J. S. Siegel, *Angew. Chem.* **1994**, *106*, 1808 – 1810; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1721 – 1723.

[32] M. Trætteberg, P. Bakken, H. Hopf, T. Hopfner, *J. Mol. Struct.* **1998**, *445*, 99 – 105.

[33] A. Stanger, E. Tkachenko, *J. Comput. Chem.* **2001**, *22*, 1377 – 1386.

[34] The Julg parameter[34a] may be used to estimate aromaticity on the basis of bond-length alternation.[34b] For the central rings of compounds **4** and **5**, the Julg parameter is in the range 0.98–1.00, that is, close to 1, and corresponds to nearly complete bond-length equalization. This result may suggest aromaticity of the central six-membered ring. However, this equalization is a consequence of a small negative SIBL and can not be used as evidence for the aromaticity of compounds **4** and **5**. a) B. Goldfuss, P. von R. Schleyer, F. Hampel, *Organometallics* **1996**, *15*, 1755 – 1757; b) T. M. Krygowski, M. K. Cyranski, *Chem. Rev.* **2001**, *101*, 1385 – 1419.

[35] For the photoelectron spectrum of compound **4**, see: P. Rademacher, C. Heinemann, S. Jansch, K. Kowski, M. E. Weiss, *Spectrochim. Acta Part A* **2000**, *56*, 1179 – 1190; $IP_1 = 7.76$ eV.

[36] Part of the blue shift results from the substitution of hydrogen atoms for carbon atoms at the 3- and 4-positions of the heterocycles. Indeed, the absorption calculated at the TD-B3LYP/6-31G(d) level for 3,4-dimethylthiophene (213.6 nm) is blue shifted by 0.12 eV relative to the calculated absorption for thiophene (209.2 nm). Thus, we can estimate a conjugation of 0.37 eV between thiophene rings in **4** on the basis of the UV spectra.

[37] The second calculated observable transition for compound **4** is at 256 nm. For compound **5**, the corresponding calculated absorptions are at 319 and 268 nm. The calculated intensity (oscillator strength) of the second transition in **4** is 4.7 times stronger than that of the first transition, whereas for **5** the calculated intensity of the second transition is 3.7 times stronger than that of the first transition. These results are in excellent agreement with the data in Figure 2.

[38] The antibonding combination contributes to the long *exo* C–C bonds in compounds **4** and **5**.

[39] The X-ray crystal structure of a charge-transfer complex of **4** with tetrafluorotetracyanoquinonedimethane ($TCNQF_4$), $\mathbf{4}_2TCNQF_4$, has been reported: T. Sugano, T. Hashida, A. Kobayashi, H. Kobayashi, M. Kinoshita, *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2303. In agreement with Figure 3, the transfer of half an electron from compound **4** to $TCNQF_4$ results in an elongation of the *endo* and *exo* C–C bonds in compound **4**, whereas the exocyclic C=C bonds remain practically unchanged. The *endo*, *exo*, and exocyclic C–C bonds in $\mathbf{4}_2TCNQF_4$ have an average length of 1.427, 1.451, and 1.368 Å, respectively, and are thus 0.012, 0.012, and 0.003 Å shorter than the corresponding bonds in **4**.

[40] Compounds **4** and **5** can also be considered to have annulene character. The additional UV absorption at around 320 nm might be attributable to a contribution from an annulene-type structure. Unfortunately, we are unable to estimate such a contribution. Alternatively, compounds **4** and **5** can be described as weakly coupled thiophene and selenophene rings, respectively. Support for this interpretation can be found in the UV/Vis spectra, the NICS values, and the X-ray crystallographic data. However, both **4** and **5** obey the well-accepted definition of radialenes.[1,2]

[41] The trends observed in the HOMO energies calculated for compounds **4**–**7** are similar to those observed in the oxidation potentials measured for these compounds; similar trends are observed in the calculated HOMO–LUMO gaps to those observed in the UV absorption of these compounds.[17]

