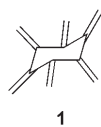


Planar [6]Radialenes: Structure, Synthesis, and Aromaticity of Benzotriselenophene and Benzotrithiophene**

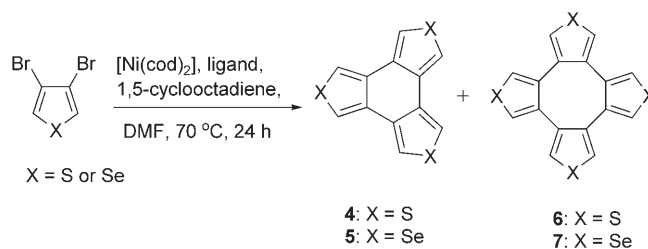
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Radialenes (e.g. [6]radialene, **1**) are a relatively modern class of alicyclic hydrocarbons in which all carbon atoms in the ring are sp^2 hybridized and there are as many exocyclic double bonds as possible.^[1,2] The first radialene, 7,8,9,10,11,12-hexamethyl[6]radialene, 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]



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'']trisenophene (**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.

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 cyclo-oligomerization. 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 (Ph₃P 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

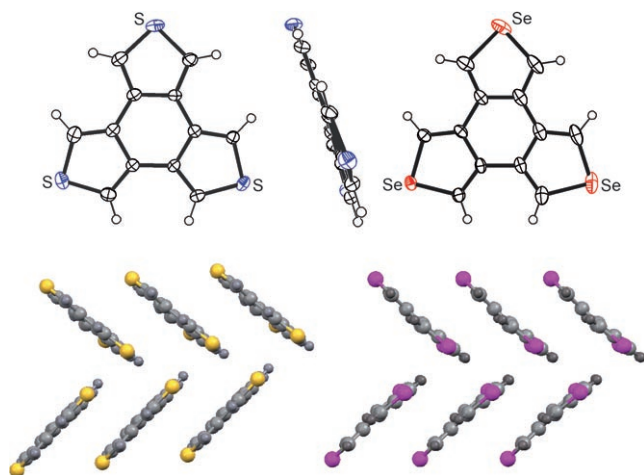


Figure 1. X-ray crystal structures (top: ORTEP diagrams; bottom: packing pattern) of compounds **4** (left; two molecules are shown in the ORTEP diagram)^[20] and **5** (right). See Table 2 for bond lengths and bond angles. In both structures, stacking molecules are positioned on the same translation 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 [°]	
	<i>endo</i> ^[b]	<i>exo</i> ^[b]	exocyclic C=C ^[b]	<i>endo</i> ^[c]	<i>exo</i> ^[c]
4 ^[d]	1.439 (1.449)	1.463 (1.462)	1.371 (1.373)	112.0 (112.1)	128.0 (127.9)
5 ^[d]	1.451 (1.453)	1.463 (1.466)	1.363 (1.370)	114.3 (114.0)	125.7 (126.0)
2 ^[e]	1.440 (1.438)	1.452 (1.466)	1.368 (1.372) ^[f]	112.3 (112.7) ^[f]	135.4 (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 sp²-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(sp²)-C(sp²) 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 sp² 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(sp²)–C(sp²) 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(sp²)–C(sp²) 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]

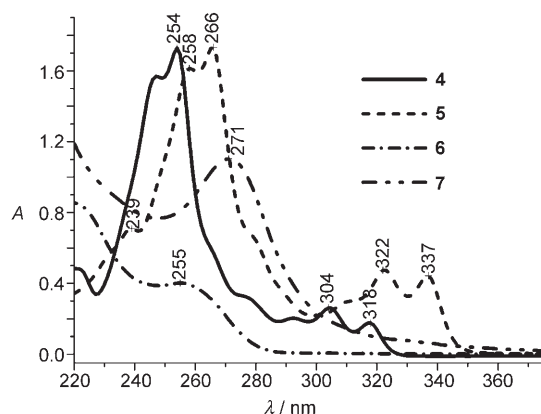


Figure 2. UV/Vis absorption spectra of compounds **4–7**.

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

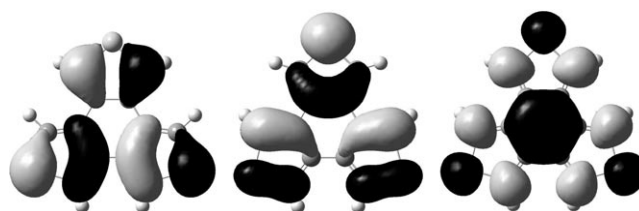


Figure 3. HOMO–1 (left), HOMO (middle), and LUMO (right) of compound **4** (at the B3LYP/6-31G(d) level).

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]

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 sp² 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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- [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.
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- [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.
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- [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 tetrafluorotetracyanoquinonodimethane (TCNQF₄), **4**₂TCNQF₄, 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 TCNQF₄ 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 **4**₂TCNQF₄ 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]