Radialenes

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 sp² 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 struc-

tures 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 twistedenvelope 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 condensedthiophene-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]

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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. Herein, we report the efficient synthesis, X-ray crystal structures, and characterization of previously unknown benzo[1,2-c:3,4-c':5,6c'']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.

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 Ph₃P 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, CHCl₃, 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.

х	Ligand	Yield of 4 (X = S) or 5 (X = Se) [%] ^[a]	Yield of 6 (X = S) or 7 (X = Se) [%] ^[a]
s	Ph₃P	40	40
S	2,2'-bipyridyl	14	60
Se	Ph₃P	50	10
Se	2,2'-bipyridyl	30	5

[a] Yield of the isolated product.



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 $[Ni(cod)_2]$ 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 [°]	
	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 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 sixmembered 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 sp²hybridized carbon atoms. For comparison, the interplanar distance between tetracene units in rubrene (record high mobility has been demonstrated for rubrene in organic fieldeffect 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 $63^{\circ[25b]}$ 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.

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	Centra	al 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]

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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 nonaromatic [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 sixmembered 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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- [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 results are in excellent agreement with the data in Figure 2.
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- [39] The X-ray crystal structure of a charge-transfer complex of 4 with tetrafluorotetracyanoquinonedimethane (TCNQF₄),
 4₂TCNQF₄, 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_2 TCNQF₄ 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]

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