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Heterohexahelicenes

A Simple, Serendipitous Synthesis of Heterohexahelicenes

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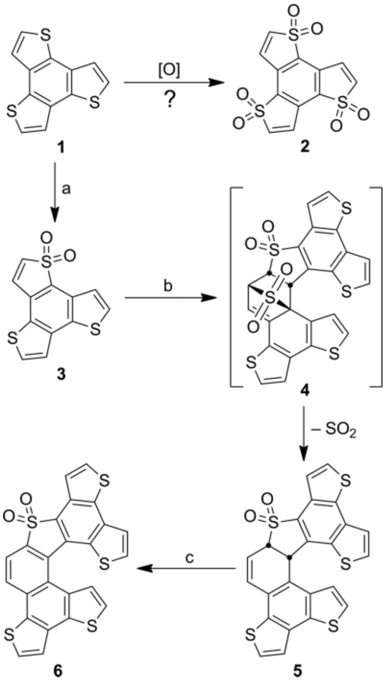
Abstract: Oxidation of benzo[1,2-*b*:3,4-*b*′:5,6-*b*′′]trithiophene (**1**) with MCPBA at room temperature gives the corresponding monosulfone **3**. This material readily undergoes a Diels–Alder dimerization with extrusion of SO_2 to form the dihydroheterohelicene **5**. This, in turn, is easily converted into the heterohelicene **6** in a one-pot NBS bromination and elimination. In a similar manner, oxidation of phenanthro[9,10-*b*]thiophene (**12**) gives the dihydroheterohelicene **13**, and bromination/elimination forms the corresponding heterohelicene **8**. The X-ray structures of compounds **5**, **6**, and **13** are reported, as well as computational studies that illuminate the unusual regiochemical outcome of the dimerization reactions.

Introduction

Benzo[1,2-*b*:3,4-*b*′-5,6-*b*′′]trithiophene (**1** or C_{3h}-BTT, Scheme 1), is trivially prepared from phloroglucinol in two steps.[1] This and the six other isomers of benzotrithiophene are calculated to be excellent electron donors,[2] and we have prepared a variety of charge transfer complexes by the crystallization of **1** with organic acceptors.[3] In principle, C_{3h}-BTT might also be used as a triple dienophile in Diels–Alder reactions for the preparation of large, C_3-symmetric molecular propellers, a class of molecules that has interested us for decades.[4] However, all our attempts at such reactions, even under the most extreme conditions, have returned only starting materials or decomposition products. A possible solution is to oxidize **1** to the trisulfone **2**, which destroys the aromaticity of the thiophene rings and activates the peripheral double bonds as dienophiles.



Scheme 1. Conditions: (a) MCPBA, CH_2Cl_2, r.t.; (b) toluene, 110 °C; (c) NBS, CCl_4, light, reflux; then Et_3N, reflux.

Oxidation of **1** may be accomplished with peracids, but trisulfone **2** remains elusive. We report herein the formation of the monosulfone **3**, which, even under mild conditions, dimerizes and extrudes sulfur dioxide to give the dihydroheterohexahelicene **5**. We report the conversion of **5** to the heterohexahelicene **6** and the X-ray structures of compounds **5** and **6**. We also report a similar synthesis of heterohexahelicene **8** (Scheme 3) from phenanthro[9,10-*b*]thiophene (**12**) and computational studies to elucidate the regiochemical preference observed in these reactions.

Results and Discussion

When compound **1** was treated with MCPBA at room temperature for an hour, several products were formed.[5] Careful fractionation by preparative TLC eventually yielded the dioxide **3**, which was first identified by its simple ^1H NMR spectrum: two pairs of doublets, with each doublet integrating to 1 H, and a singlet with a 2 H integral, apparently due to the accidental isochrony of the resonances that would otherwise have been a third pair of doublets. HRMS analysis confirmed the formula as $C_{12}H_6O_2S_3$, but we wished unambiguously to determine the structure by X-ray crystallography.

Recrystallization of **3** from $CHCl_3$/EtOH gave crystals suitable for X-ray analysis, but the crystal proved to be composed of the dimerization product **5**. The molecular structure of **5** is illus-

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trated in Figure 1. Obviously, this structure is incompatible with the simple NMR spectrum of **3**, and we supposed at first that the structure was of an anomalous crystal: a trace but highly crystalline impurity in our sample of compound **3**. However, subsequent experiments showed that compound **5** is formed in substantial amounts in every oxidation of **1**, and when the sulfone **3** is heated, it is readily converted into the dimeric adduct **5**. In the case of the X-ray sample, either the heating of the solution prior to crystallization, or the subsequent concentration of the solution by evaporation, was sufficient to promote the Diels–Alder dimerization of **3** to **4** (Scheme 1) and the extrusion of SO_2 to give **5**. The structure of **5** is interesting in that two aromatic polycycles are fixed at essentially right angles; in our experience this is an unusual molecular conformation.

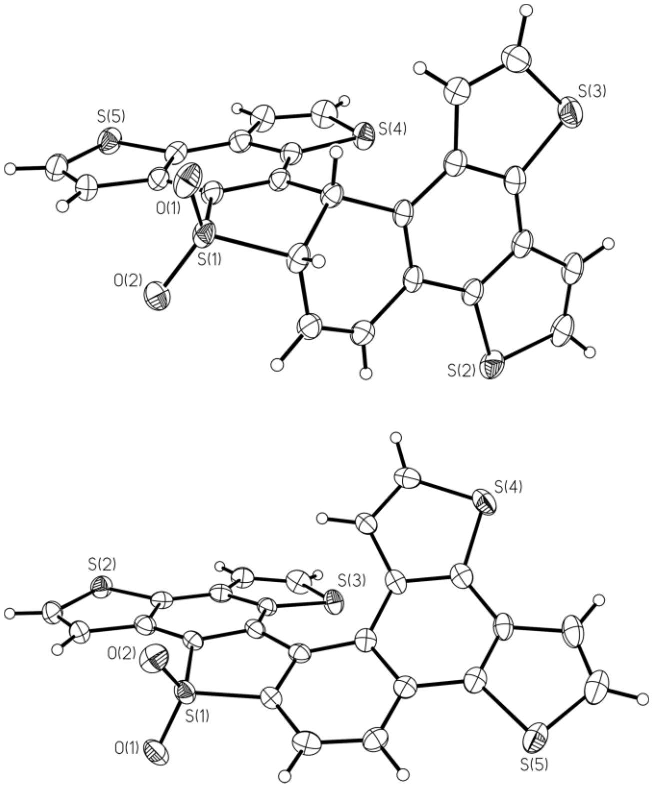
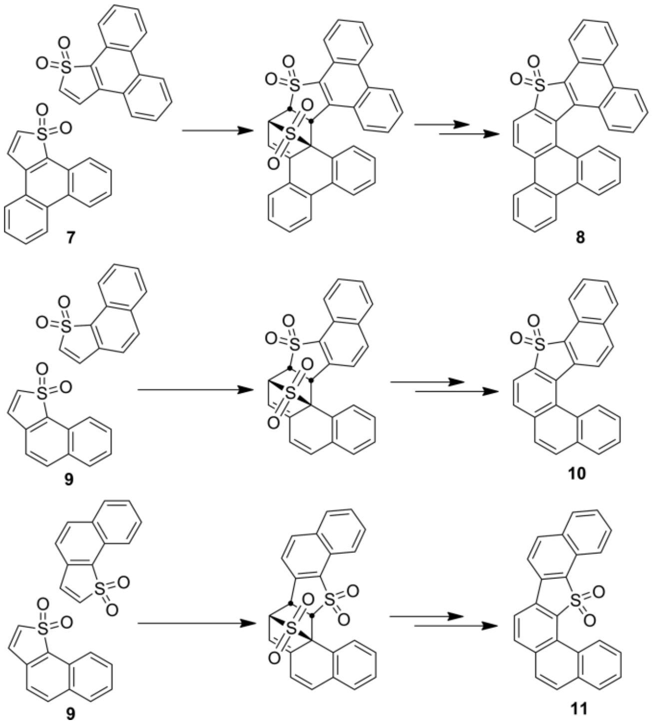


Figure 1. Molecular structures of compounds **5** (above) and **6** (below). Thermal ellipsoids are set at 50 % probability.

Compound **5** is a dihydroheterohexahelicene, and conversion to the heterohexahelicene **6** proved to be quite simple. When **5** is heated with DDQ in benzene, it is only very slowly dehydrogenated to **6**, and the reaction is “messy” at best. Much better results are obtained by NBS bromination of **5** followed by addition of triethylamine to the reaction mixture to promote elimination of HBr to give **6**. Single crystals of compound **6** formed readily from concentrated solutions in CH_2Cl_2, and the molecular structure of **6** is also illustrated in Figure 1.

Numerous thiaheterohelicenes have been prepared, but the sulfur substitution pattern in compound **6** seems to be unknown. As far as we can tell, all previous syntheses of similar thiaheterohelicenes have employed the reactions of heterocyclic aldehydes with heterocyclic Wittig reagents followed by photocyclization of the resulting diarylethylenes.[6,7] At first, we thought that we had found a new, general synthesis of thiaheterohelicenes by the dimerization of benzannulated thiophene dioxides, but a more careful analysis shows that a triphenylene-like structure is required for this approach to succeed, as may be seen in Scheme 2.

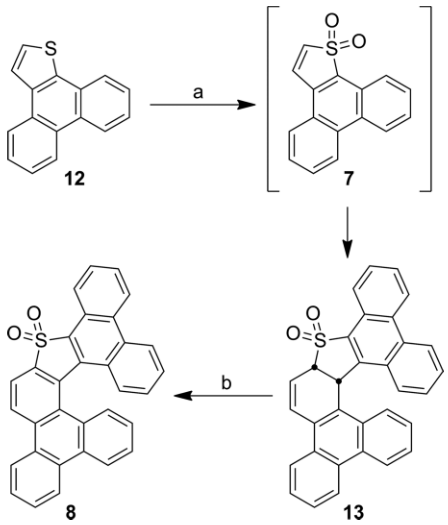


Scheme 2. Dimerization pathways for benzannulated thiophene dioxides.

For example, if the Diels–Alder dimerization of phenanthro[9,10-*b*]thiophene dioxide (**7**) proceeds with the same regiochemistry as the dimerization of **3**, then the heterohelicene **8** will be the result. However, for the dimerization of naphtho[1,2-*b*]thiophene dioxide (**9**), both the *syn* (**9** to **10**) and *anti* (**9** to **11**) regiochemical outcomes fail to yield true heterohelicenes.

We therefore prepared heterohelicene **8** to verify that the formation of compound **5** from **3** was not just a single, anomalous reaction. Phenanthro[9,10-*b*]thiophene[8] (**12**, Scheme 3) proved to be significantly more resistant to oxidation than benzotrithiophene **1**. Treatment of **12** with MCPBA in CH_2Cl_2 at room temperature gave no reaction, but treatment with MCPBA in refluxing toluene for 24 hours gave the dihydroheterohelicene **13** in 15 % purified yield. The bulk of the remaining material was unreacted **12**, and the dioxide **7** itself was not found in the reaction mixture. The latter result is not surprising, given that the temperature was much higher than that required to promote its Diels–Alder dimerization.

Single crystals were obtained for compound **13**, and its molecular structure is illustrated in Figure 2. As expected, the *syn* adduct was formed. NBS bromination of **13**, followed by treatment with triethylamine, gave the heterohelicene **8** in 66 % yield, demonstrating that, at least for the limited set of triphenylene-shaped benzannulated thiophenes, this procedure is reliable for heterohelicene synthesis.



Scheme 3. Conditions: (a) MCPBA, toluene, reflux; (b) NBS, CCl_4, light, reflux; then Et_3N, reflux.

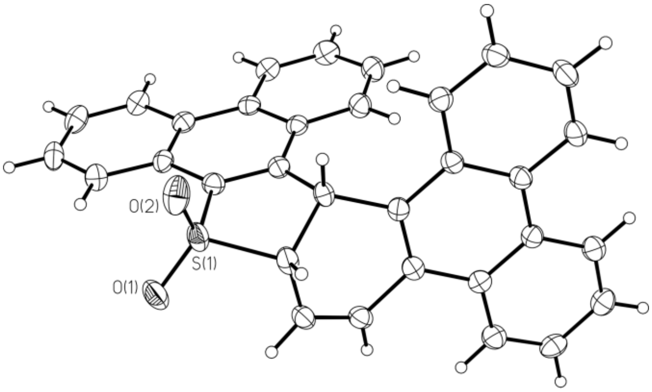
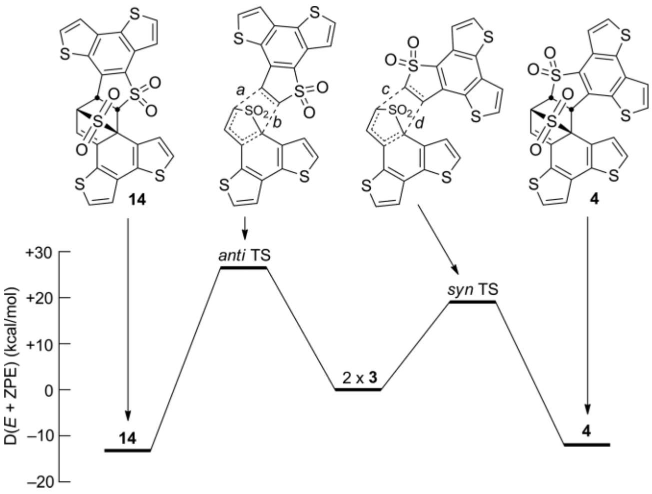


Figure 2. Molecular structure of compound **13**. Thermal ellipsoids are set at 50 % probability.



Scheme 4. Calculated reaction coordinates for the Diels–Alder dimerization of compound **3** at the B3PW91/6-311++G(2d,p) level of theory.

At first glance, the observed dimerization of **3** to give the more crowded *syn* adduct **4** is unexpected. Indeed, at the B3PW91/6-311++G(2d,p) level of theory, Diels–Alder adduct **4** is 1.2 kcal/mol less stable than the *anti* adduct **14** (Scheme 4). However, the energy of the transition state leading to **4** is 7.0 kcal/mol lower than that for **14**, explaining the regiochemical preference (all calculations are for the *endo* addition products illustrated in Scheme 4). There is no possibility of a retro-Diels–Alder reaction of **4**, and eventual equilibration to the more stable adduct **14**, because of rapid loss of SO_2 from the initial adduct.

The reason for this difference, however, is less obvious from the calculations. The HDFT-calculated *syn* transition state is highly asynchronous, with the bonding from the dienophile to the central ring of the diene barely begun (a distance of 3.164 Å for bond *d*, Scheme 4), while the carbon atoms at the other end of the reacting π-systems are strongly interacting (a distance of 1.970 Å for bond *c*). In contrast, the *anti* transition state structure is conventional, with similar distances for the incipient bonds at both ends of the interacting π-systems (2.156 Å and 2.312 Å for bonds *b* and *a*, respectively). Both structures are illustrated in the Supporting Information.

Why should the highly asynchronous, *syn* transition state be preferred? We might ascribe the preference to the old standby, secondary orbital overlap, but a glance at the transition state structures shows that the extra rings in these molecules are rather far apart. Perhaps the greater stability of the *syn* transition state can be ascribed to two other factors. First, the less-interacting carbon of the dienophile and one of the non-interacting carbons of the diene are essentially benzylic radicals in the *syn* transition state, whereas no such stabilization is present in the *anti* transition state. Second, in the *syn* transition state, both central rings retain their aromaticity (since the distance *d* is so long), but in the *anti* transition state, the central ring of the diene must have decreased aromaticity (one of the carbons is significantly pyramidalized). Of course, the quantum calculations sum the contributions of many factors not obvious to a chemist's glance at the transition state structures, and it is perhaps best not to reduce the observed preference to any single factor.

Compounds **5**, **6**, **8**, and **13** are chiral molecules and likely to be configurationally stable, and thus there is the possibility that they might spontaneously resolve upon crystallization. Unfortunately, **5**, **6**, and **13** crystallize in the centric space groups $P2_1/n$, $P2_1/n$, and $C2/c$, respectively, and therefore the crystals contain both enantiomers. However, there was some doubt about the configurational stability of helicene **6**. Hexahelicene itself has a high barrier to racemization ($\Delta G^{\ddagger}_{rac}$ = 36.2 kcal/mol[9]), but a some simple heterohexahelicenes containing two thiophene rings are reported to have much reduced barriers ($\Delta G^{\ddagger}_{rac}$ = 22–24 kcal/mol[7a]). Would compound **6**, containing *three* five-membered rings among the six rings of the helicene, even be resolvable?

A small amount of helicene **6** was resolved by supercritical fluid chromatography on a chiral support (Chiralcel OZ-H, 60 % ethanol/CO_2 at 100 bar). The resolved enantiomers appeared to be stable at room temperature, but racemized with $t_{1/2}$ = 7.8 hours at 60 °C. (See the Supporting Information for the resolution and racemization studies.) This corresponds to a free energy of activation of 26.6 kcal/mol and a marginal degree of configurational stability at room temperature ($t_{1/2}$ ca. 1 month at 25 °C).

Conclusion

As noted previously, the synthesis of benzotrithiophene **1** is simple,[1] and other, higher-yielding, although less convenient syntheses of **1** exist.[10] In addition, two recent syntheses of phenanthrothiophene **12** make it readily available as well.[11] The oxidation and dimerization of these molecules to the dihydroheterohelicenes **5** and **13** is facile, if not high-yielding, and conversion to the corresponding heterohelicenes is a one-pot transformation. Whether this approach can be adapted for the synthesis of larger heterohelicenes remains to be seen, but the syntheses of the precursors for such reactions will likely not be so easy as the preparations of **1** and **12**.

Experimental Section

Benzo[1,2-*b*:3,4-*b*′-5,6-*b*″]trithiophene 1,1-dioxide (3) and Dihydroheterohelicene 5. C_{3h}-BTT (**1**, 0.10 g, 0.41 mmol) was dissolved in CH_2Cl_2 (10 mL), and MCPBA (0.19 g, 1.1 mmol) was added. After stirring at room temperature for 1 h, the solution was washed with 10 % $NaHCO_3$ (40 mL) followed by water. The organic phase was dried with Na_2SO_4 and concentrated, and the crude product was fractionated by silica gel preparative TLC (solvent, 9:1 CH_2Cl_2/hexanes). The bands with R_f 0.48 and R_f 0.55 were isolated to yield, respectively, compound **3** as light yellow solid (7.7 mg, 28 µmol, 7 %) and compound **5** as off-white crystals (12.7 mg, 26 µmol, 13 %). For **3**: m.p. behavior: gradually darkens above 115 °C, gradually becomes tarry above 220 °C, is not fully liquefied at 300 °C; ^1H NMR (300 MHz, CD_2Cl_2) δ = 6.91 (d, *J* = 7 Hz, 1 H), 7.59 (d, *J* = 7 Hz, 1 H), 7.76 (d, *J* = 5 Hz, 1 H), 7.82 (s, 2 H), 7.93 (d, *J* = 5 Hz, 1 H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ = 120.1, 122.2, 123.4, 129.3, 130.2, 130.4, 131.2, 131.4, 137.6, 137.7 (10 of 12 expected resonances); HRMS (ESI-TOF) *m/z* 278.9603 (M + H), calcd. for $C_{12}H_7O_2S_3$ 278.9608. An attempt to crystallize compound **3** from $CHCl_3$/EtOH yielded a single crystal of the dimer **5**. In a separate experiment, a sample of pure compound **3** (31 mg, 0.11 mmol) was dissolved in toluene (2 mL), and the solution was heated at 110 °C in a screw-capped tube overnight. The solution was cooled to room temperature, and the solvent was removed by rotatory evaporation. Recrystallization of this material from CH_2Cl_2/EtOH gave pure **5** (9.1 mg, 18 µmol, 34 %). For **5**: m.p. behavior: darkens and becomes tarry above 240 °C, is not fully liquefied at 300 °C; ^1H NMR (300 MHz, CD_2Cl_2) δ = 4.86 (m, 1 H), 5.92 (dd, *J* = 6 Hz, 1 Hz, 1 H), 6.37 (ddd, *J* = 10 Hz, 2 Hz, 1 Hz 1 H), 6.98 (dd, *J* = 10 Hz, 3 Hz, 1 H), 7.48 (d, *J* = 5.5 Hz, 1H), 7.52 (d, *J* = 5 Hz, 1 H), 7.76 (m, 5 H), 7.97 (d, *J* = 5 Hz, 1 H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ = 39.6, 65.3, 120.2, 120.3, 120.9, 121.4, 122.2, 122.8, 124.3, 126.0, 127.1, 128.0, 128.2, 128.3, 129.1, 131.7, 131.8, 132.9, 134.3, 134.8, 135.0, 136.7, 138.32, 138.35 (24 of 24 expected resonances observed); HRMS (ESI-TOF) *m/z* 492.9513 (M + H), calcd. for $C_{24}H_{13}O_2S_5$ 492.9519.

Heterohelicene 6. Compound **5** (19.6 mg, 39.8 µmol) and NBS (7.1 mg, 40 µmol) were suspended in CCl_4 (6 mL), and the mixture was heated at reflux overnight under a 45 W tungsten lamp. Triethylamine (3 mL) was added, and the reaction was heated at reflux for another 6 h. The resulting solution was washed with 1 *M* HCl (30 mL) followed by water. The organic phase was dried with Na_2SO_4 and concentrated. The crude product was fractionated by silica gel preparative TLC (solvent, 4:1 CH_2Cl_2/hexanes) and the band with R_f 0.60 was isolated to yield compound **6** as a bright yellow solid (8.9 mg, 18 µmol, 46 %); m.p. > 300 °C. ^1H NMR (300 MHz, CD_2Cl_2) δ = 7.28 (d, *J* = 5 Hz, 1 H), 7.50 (d, *J* = 5 Hz, 1 H), 7.68 (d, *J* = 5 Hz, 1 H), 7.74 (d, *J* = 5 Hz, 1 H), 7.78 (d, *J* = 5 Hz, 1 H), 7.84 (d, *J* = 5 Hz, 1 H), 7.88 (d, *J* = 5 Hz, 1 H), 8.00 (d, *J* = 5 Hz, 1 H), 8.02 (d, *J* = 8 Hz, 1 H), 8.39 (d, *J* = 8 Hz, 1 H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ = 116.8, 120.7, 121.0, 121.6, 122.9, 123.4, 126.2, 128.0, 128.5, 128.8, 129.0, 129.2, 129.4, 130.5, 131.2, 132.0, 132.4, 132.6, 134.3, 134.6, 136.6, 137.8, 137.9, 138.9 (24 of 24 expected resonances); HRMS (ESI-TOF) *m/z* 490.9353 (M + H), calcd. for $C_{24}H_{11}O_2S_5$ 490.9362. A single crystal suitable for X-ray analysis was obtained from CH_2Cl_2.

Dihydroheterohelicene 13. A solution of phenanthrol[9,10-*b*]thiophene[8] (**12**, 0.050 g, 0.21 mmol) and MCPBA (0.13 g, 0.75 mmol) in toluene (12 mL) was heated at reflux for 24 hours. The reaction was quenched with excess 10 % $NaHCO_3$, the organic phase was separated, and it was dried with Na_2SO_4. The solvent was removed, and the dark green residue was fractionated by preparative TLC (solvent, 3:1 CH_2Cl_2/hexanes). The band with R_f 0.3 was isolated and recrystallized twice from CH_2Cl_2 to yield compound **13** as white crystals (7.5 mg, 16 µmol, 15 %); m.p. > 300 °C. ^1H NMR (500 MHz, CD_2Cl_2) δ = 4.71 (m, 1 H), 6.19 (d, *J* = 6 Hz, 1 H), 6.62 (ddd, *J* = 10 Hz, 2 Hz, 1 Hz, 1 H), 6.88 (ddd, *J* = 8 Hz, 7 Hz, 1 Hz, 1 H), 7.37 (dd, *J* = 9 Hz, 1 Hz, 1 H), 7.54 (ddd, *J* = 8 Hz, 7 Hz, 1 Hz, 1 H), 7.59 (dd, *J* = 10 Hz, 3 Hz, 1 H), 7.74 (ddd, *J* = 8 Hz, 7 Hz, 1 Hz, 1 H), 7.77 (ddd, *J* = 8 Hz, 7 Hz, 1 Hz, 1 H), 7.84 (m, 4 H), 8.27 (d, *J* = 8 Hz, 1 H), 8.48 (d, *J* = 8 Hz, 1 H), 8.72 (d, *J* = 8 Hz, 1 H), 8.77 (m, 2 H), 8.93 (dd, *J* = 8 Hz, 1 Hz, 1 H), 8.97 (dd, *J* = 8 Hz, 1 Hz, 1 H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ = 38.3, 63.8, 123.2, 123.32, 123.34, 123.38, 123.5, 123.7, 123.8, 124.6, 126.2, 126.8, 127.0, 127.18, 127.22, 127.38, 127.42, 127.9, 128.2, 128.3, 128.46, 128.54, 128.56, 130.1, 130.5, 130.6, 131.2, 131.3, 132.3, 133.2, 136.0 (31 of 32 expected resonances); HRMS (ESI-TOF) *m/z* 469.1253 (M + H), calcd. for $C_{32}H_{21}O_2S$ 469.1262. A single crystal suitable for X-ray analysis was obtained from CH_2Cl_2.

Heterohelicene 8. Compound **13** (10.2 mg, 21.8 µmol) and NBS (3.9 mg, 22 µmol) were suspended in CCl_4 (6 mL) and heated at reflux overnight under a 45 W tungsten lamp. Triethylamine (4 mL) was added and the reaction was heated at reflux for another 5 hours. The organic solution was diluted with $CHCl_3$ and washed with excess 1 *M* HCl and water. The organic phase was dried with Na_2SO_4 and concentrated. The crude product was fractionated by silica gel preparative TLC (solvent, 1:1 CH_2Cl_2/hexane), and the band with R_f 0.18 was isolated to yield compound **8** as an orange powder (6.7 mg, 14 µmol, 66 %); m.p. > 300 °C. ^1H NMR (500 MHz, CD_2Cl_2) δ = 6.92 (ddd, *J* = 8 Hz, 7 Hz, 1 Hz, 1 H), 7.09 (ddd, *J* = 8 Hz, 7 Hz, 1 Hz, 1 H), 7.56 (ddd, *J* = 8 Hz, 7 Hz, 1 Hz, 1 H), 7.60 (dd, *J* = 8 Hz, 1 Hz, 1 H), 7.67 (m, 2 H), 7.84 (m, 2 H), 7.92 (m, 2 H), 8.17 (d, *J* = 8 Hz, 1 H), 8.59 (d, *J* = 8 Hz, 1 H), 8.62 (m, 1 H), 8.67 (dd, *J* = 8 Hz, 1 Hz, 1 H), 8.73 (dd, *J* = 8 Hz, 1 Hz, 1 H), 8.77 (d, *J* = 8 Hz, 1 H), 8.83 (d, *J* = 8 Hz, 1 H), 8.86 (m, 1 H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ = 118.2, 123.49, 123.53, 123.55, 123.61, 124.0, 124.3, 124.5, 124.8, 125.3, 125.4, 126.1, 128.1, 128.2, 128.5, 128.78, 128.86, 128.89, 128.92, 129.0, 129.1, 129.5, 130.3, 130.8, 131.0, 132.0, 132.5, 133.0, 133.1, 136.1, 139.2 (31 of 32 expected resonances); HRMS (ESI-TOF) *m/z* 467.1101 (M + H), calcd. for $C_{32}H_{19}O_2S$ 467.1106.

Computational studies. All HDFT calculations were performed using Gaussian 09,[12] and its built-in default parameters wave function and gradient convergence were employed, but integrals were calculated using the ultrafine grid for compatibility with calculations performed using Gaussian 16. All HDFT calculations included full geometry optimizations and analytical frequency calculations at the B3PW91/6-311++G(2d,p) level of theory,[13–15] with transition states located by means of the QST3 option.

Crystallographic Data. CCDC 1947218 (for **5**), 1947219 (for **6**), and 1947220 (for **13**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Acknowledgments

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Keywords: Heterohelicenes · Thiophene dioxides · Diels–Alder reactions

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[5] No starting material remains at the end of this reaction. Several products are formed in addition to compounds **3** and **5** (that are the subject of this paper), but most have complex NMR spectra. The single exception has been *tentatively* identified as the disulfone on the basis of its proton NMR spectrum [^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.01 (d, J = 7 Hz, 1 H), 7.06 (d, J = 7 Hz, 1 H), 7.57 (d, J = 7 Hz, 1 H), 7.75 (d, J = 7 Hz, 1 H), 7.83 (d, J = 6 Hz, 1 H), 8.12 (d, J = 6 Hz, 1 H)]. No compound with the expected proton NMR spectrum of **2** (a single pair of doublets) has been observed at any time.
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