# Triphenyleno[1,12-*bcd*:4,5-*b*′c′d′:8,9-*b*″c″d″]trithiophene: the first bowl-shaped heteroaromatic

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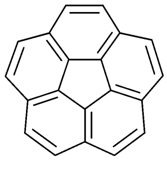
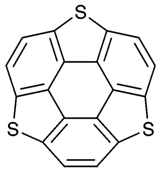
**The title compound has been synthesized, and its unique bowl-shaped molecular structure and electronic spectra have been elucidated.**

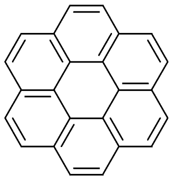
The discovery of buckminsterfullerene has stimulated much interest in the chemistry of bowl-shaped polycyclic aromatic hydrocarbons, such as corannulene **1**.[1–5] Such bowl-shaped compounds can be expected to exhibit unique physicochemical properties related to the buckminsterfullerene surface. Although polycyclic heteroaromatics are of current interest for advanced materials,[6] no heteroaromatics with bowl curvature have been reported to the best of our knowledge.[7] Triphenyleno[1,12-*bcd*:4,5-*b*′c′d′:8,9-*b*″c″d″]trithiophene **2**, so far unknown, is remarkable because the electronic structure of **2** is similar to that of highly symmetrical coronene **3**. However, **2** contains severe strain in the molecular structure due to the three five-membered thiophene rings in the periphery, and accordingly, unlike planar coronene,[8] is expected to adopt a bowl-shaped structure. We now report the synthesis, molecular structure and spectroscopic properties of **2** as the first bowl-shaped heteroaromatic.



**1**



**2**



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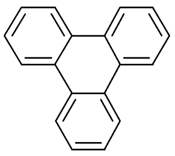

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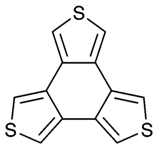
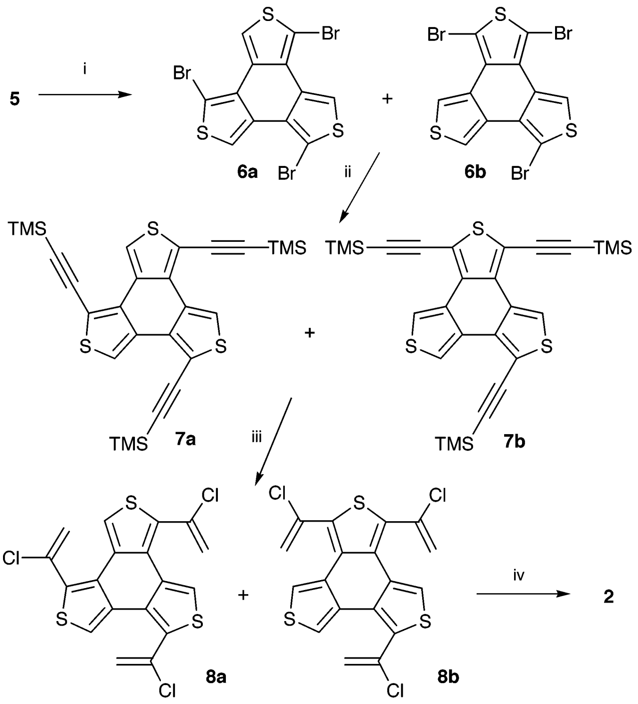


**5**

The synthesis of **2** was previously attempted by inserting sulfur bridges in the bay regions of triphenylene **4**; although the mono- and di-bridged species were successfully made, the tri-bridged species **2** was not found.[9] The difficult synthesis of **2** is presumably due to its strained structure. Our successful synthetic route is based on tribenzannulation of benzotrithiophene **5** by a flash-vacuum pyrolytic method, which was applied recently to a short access to strained aromatic systems, such as corannulene[2,4,5] and more recently to thiophene-containing heteroaromatic systems.[10] As shown in Scheme 1, **5**[11] was treated with NBS (3 equiv.) to give the tribromo derivative **6**, which was subsequently converted to the trimethylsilylethynyl derivative **7** by the Sonogashira reaction (two step yield 53%). An NMR analysis indicated that the product comprised two regioisomers **7a** and **7b** in a ratio of about 1:5. Other possible isomers which accommodate two substituent groups in the same bay region were not formed. Treatment of **7** with HCl gave the tris(chlorovinyl) compound **8** (33% yield), which was then subjected to flash vacuum pyrolysis under the conditions of 1000 °C and 0.005 Torr to afford the desired compound **2** in 35% yield.†



**Scheme 1** *Reagents and conditions*: i, NBS (3.0 equiv.), DMF, room temp.; ii, $TMSC\equiv CH$, $Pd(PPh_3)_4$, CuI, $NEt_3$, reflux; iii, conc. HCl, AcOH, 80 °C; iv, 1000 °C, 0.005 Torr, $N_2$ flow.

As shown in Fig. 1, an X-ray crystallographic analysis of **2** clearly revealed that it has the expected bowl-shaped molecular structure,‡ which is somewhat shallow compared to corannulene.[12] The crystal structure belongs to the hexagonal

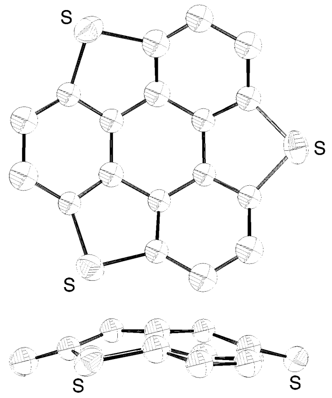


**Fig. 1** Molecular structure of **2**: top view (top) and side view (bottom).

crystal system, which is very rare for the crystal structures of organic molecules. The molecules are stacked in a concave–convex fashion, unlike corannulene but like the deeper bowl-shaped aromatic hydrocarbons,[2,5] with marked intermolecular S–S contacts.

The electronic absorption spectrum of **2** in $CH_2Cl_2$ shows a long-wavelength vibrational α-band at $\lambda_{max}$ 368 nm (log $\varepsilon$ 3.13), which, though weak as a symmetry-forbidden transition, causes yellow coloration for **2**. In addition, there are two strong bands centered at 318 (4.42) and 245 nm (4.47), assignable to p- and β-bands, respectively. The whole absorption spectrum roughly resembles that of coronene itself,[13] supporting iso-electronic structures for both compounds. In a more detailed comparison, the respective absorption bands of **2** are somewhat blue-shifted. Coincidentally **2** demonstrates a fluorescent emission at $\lambda_{max}$ 398 and 414 nm, whereas coronene fluoresces at longer wavelengths ($\lambda_{max}$ 436, 456, and 482 nm).

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## Notes and references

† *Selected data* for **2**: yellow fine needles from $CS_2$–hexane; mp > 300 °C; $\delta_H(CDCl_3)$ 8.01 (s, 6H); $\delta_C(CDCl_3)$ 122.7, 135.6, 141.0; *m/z* 318 ($M^+$) (Calc. for $C_{18}H_6S_3$: C, 67.89; H, 1.89. Found: C, 67.87; H, 1.97%).

‡ *Crystal data* for **2**: $C_{18}H_6S_3$, $M$ = 318.43, hexagonal, space group *P*6*cc* (no. 184), $a = b = 26.121(7)$, $c = 7.433(3)$ Å, $V = 4392(1)$ Å$^3$, $Z = 14$, $D_c = 1.685$ g cm$^{-3}$, $\mu$(Mo-Kα) = 5.76 cm$^{-1}$, crystal dimensions 0.85 × 0.03 × 0.03 mm$^3$. The structure analysis is based on 1820 reflections ($2\theta_{max}$ = 55°), 698 observed [$I \geqslant 2\sigma(I)$], and 126 parameters. The structure was solved by direct methods (SIR92). It was refined by full-matrix least-squares (SHELXL-93) on $F^2$ with anisotropic temperature factors for the sulfur atoms and isotropic for the carbon atoms because the number of observed reflections is not enough to refine the structure with anisotropic temperature factors for all atoms. The hydrogen atoms were not included in the refinement. The final $R$ was 0.085 [$I \geqslant 2\sigma(I)$]. The unit cell contains two independent molecules, and one molecule is located on a crystallographic 6-fold axis with disorder. Both molecules adopt virtually the same bowl-shaped structure. CCDC 182/1376. See http://www.rsc.org/suppdata/cc/1999/1859/ for crystallographic data in .cif format.

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