Synthesis, structure and properties of decakis(phenylthio)corannulene†‡

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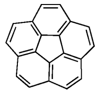
Decakis(phenylthio)corannulene has been prepared from decachlorocorannulene by direct nucleophilic substitution; electronic structure properties and the X-ray crystal structure were determined and compared to predictions made by *ab initio* quantum chemical calculations.

Decasubstitution of corannulene (**1**) reduces the depth of the bowl through steric effects around the rim, and tunes the electronic properties of the π system according to the nature of the substituents.[1] Exhaustive over-chlorination/dechlorination of corannulene yields decachlorocorannulene (**2**),[2] through which decamethyl (**3**),[3] decapentynyl (**4**),[4] decakis(alkylthio) and decakis(arylthio)-corannulenes.[2a,5] have been prepared. The electron diffraction structure of **2** as well as the crystal structure of **4** clearly display a shallower bowl,[4,6] but as predicted computationally, about 50% of the bowl depth persists compared to **1** even when the steric repulsion of persubstitution reduces the bowl-inversion barrier from *ca.* 12 to *ca.* 1 kcal mol^{-1}.[7] The strain in **4** can also be relieved by an enediyne rearrangement in which one ring of the aromatic core opens to a 10 annulene and renders the π system planar.[4] Corannulene derivatives **2–4** vary in their ability to accept/donate electrons.[2c,8] The effect of sulfur, as in decakis(phenylthio)corannulene (**5**), should be greater based on other per(R-thio)-substituted aromatics.[9] This work presents the X-ray crystal structure, quantum chemical structure and selected physical properties of **5**.

Direct nucleophilic substitution by thiophenoxide on **2** proceeds cleanly to yield **5**. Slow diffusion of methanol to a benzene solution of **5** produced red crystals suitable for X-ray crystallographic analysis.[10] The crystal structure revealed a monoclinic unit cell with symmetry $P2_1/n$. The asymmetric unit contained one molecule disordered about two molecular orientations with equal population, wherein the thiophenol units overlap, but the corannulene bowls are inverted and antiparallel to one another (Fig. 1).

Molecules of **5** adopt a crystal packing motif wherein the overlapping phenyl residues define a layer of interdigitated aryl fingers distinct from a disordered layer of corannulene bowls (Fig. 2).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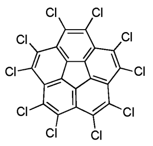

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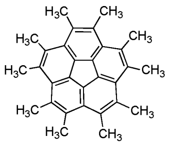

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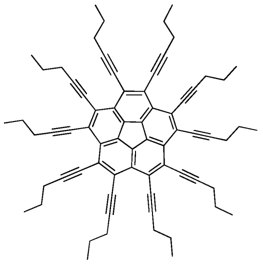
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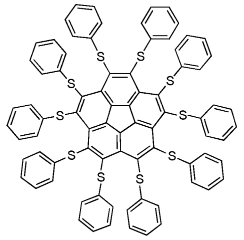

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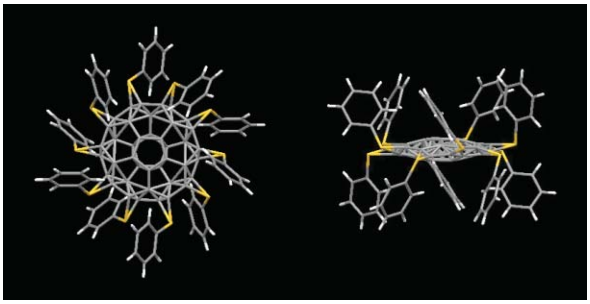

Fig. 1 Disordered molecular structure of **5** from X-ray diffraction analysis: Left – face on shows the antiparallel overlap of the corannulene cores; right – edge on shows the overlap of two bowl inversion orientations; in all cases the thiophenol units overlap with unresolvable positional disorder.

Given the molecular disorder and the reduction of molecular symmetry in the crystal, average values of chemical equivalent carbon–carbon bond lengths are reported: 1.416 Å (hub), 1.376 Å (spoke), 1.434 Å (flank), 1.384 Å (rim). The bonding pattern resembles well that of the parent **1** distorted by compression of the hub and stretching of the rim. The bowl depth in **5** is 0.320 Å (hub-to-spoke) and 0.486 Å (hub-to-rim), between 55–60% the depth of corannulene.

Absorption spectra of **5** show maxima at 200 (5.41), 375 (5.21), and 410 (4.75) nm (log e), substantially longer wavelengths than that of **1** and comparable to C_{60}.[11] No appreciable emission was detected.

Cyclic voltammetry on an acetonitrile (0.1 M tetrabutylammonium hexafluorophosphate) solution of **5** displayed fours waves at −1.22, −1.62, −2.04, and −2.28 volts *vs.* Ag/AgNO$_3$. Values for **1** under comparable conditions are −2.23 and −2.84 volts.[2c,12] The

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‡ Electronic supplementary information (ESI) available: Synthesis, crystallographic methods and computational details. CCDC reference number 748565. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b919616a

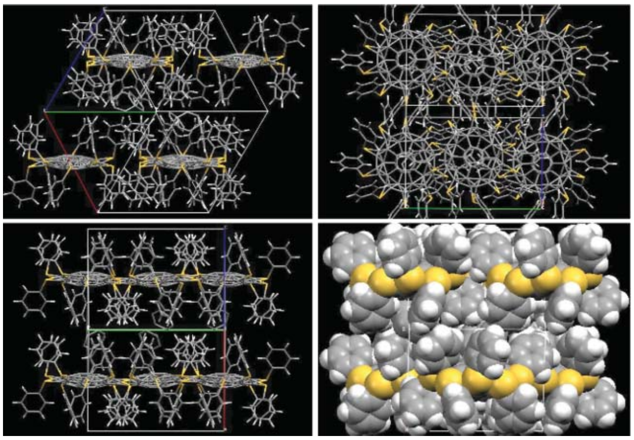

Fig. 2 Packing diagram of disordered **5**. The structure displays layered regions of aryl fingers and sulfur substituted corannulene bowls.

ease of the first reduction of **5** is on a par with the value of −1.06 volts for the first reduction of C_{60}.[13]

The electronic structure and physical properties of **5** were calculated using the DFT B98 functional (Fig. 3).[14] The computation predicts greater distortion of the rim bonds and less compression of the hub compared to corannulene: 1.414 Å (hub), 1.386 Å (spoke), 1.466 Å (flank), 1.425 Å (rim); bowl depths of 0.40 (hub-to-spoke), 0.63 (hub-to-rim). An idealized D_5 transition state to bowl inversion is calculated to be 8.28 kcal mol^{-1} higher than the C_1 conformer, including ZPE (C_1 0.0, C_5 3.67, D_5 8.28 kcal mol^{-1}).

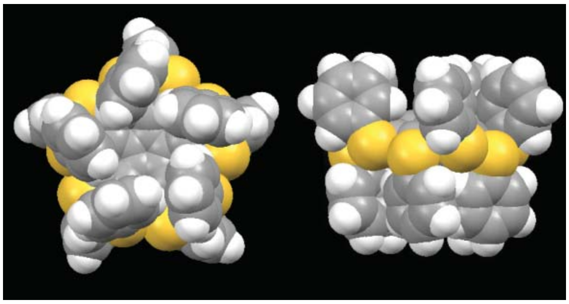

Fig. 3 *Ab initio* C_5 molecular structure of **5**. Face and edge views depicting the edge-to-face arene interactions (*cf.* Fig. 1).

Frontier molecular orbital analysis accounts for the longer wavelength absorption spectrum and lower reduction potential of **5** *vis a vis* **1**. The LUMO of **5** extends beyond the core π system to include the adjacent sulfur atoms (Fig. 4). The larger "box" correlates to lower energy transitions and lower lying radical anion states. Empirically, the smaller HOMO/LUMO gap is evidenced by the deep red color of **5** compared to the pale yellow of **1**, **2** and **3**.

The alternate up-down conformation adopted by **5** in combination with its packing in the crystal stimulates the possible use of such corannulene derivatives as ordered materials. The additional fact that **5** and cognates have a standing dipole moment, absorb light well at long wavelength and are roughly as easy to reduce as C_{60}, adds a functional component to exploit. In the area of electro-active liquid crystals, related decakis(X-thio) corannulenes have already proven this principle.[5d]

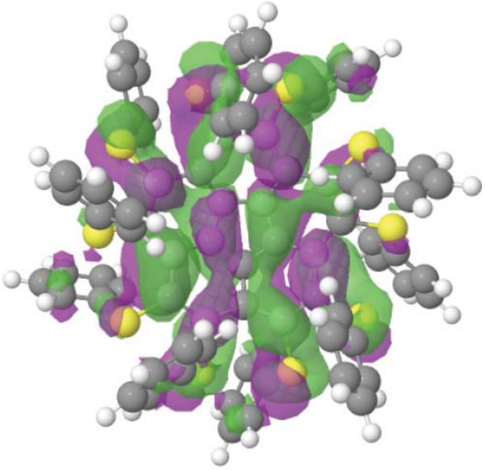

Fig. 4 LUMO of **5** (isocontour value 0.01 a.u.).

Acknowledgements

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10 A crystal of **5** was placed on a Bruker SMART 1000 CCD sealed tube diffractometer with graphite monochromated Mo-Kα radiation (0.71073 Å). The crystal was found to be monoclinic, $P2_1/n$, with unit cell dimensions of 15.227(3), 15.372(3). 16.161(3) Å, $\beta = 92.447(3)°$ and a volume of 3779.3(11) Å^3. Data were measured at 153 K and processed using SMART[10a] and SAINT[10b] software. The structure was solved by Direct Methods and Fourier techniques using SHELXTL[10c].(*a*) *Bruker SMART*, Bruker AXS Inc., Madison, WI, USA; (*b*) *Bruker SAINT*, Bruker AXS Inc., Madison, WI, USA; (*c*) G. M. Sheldrick, A short history of SHELX, *Acta Crystallogr., Sect. A*, 2008, **64**, 112–122. Additional information is contained in the Supplemental Information.
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14 Computational Methods: The conformational analyses of the molecular systems described in this study, including structural, molecular orbital, and property calculations, were carried out using GAMESS[14a]. The computations employed included several DFT methods for comparison: B97-1,[14b] B98,[14c] B97-D,[14d] and B3LYP,[14e] with Dunning's full and valence double-ζ sets supplemented with (2d,p) polarization, DZ(2d,p),[14f] and DZV(2d,p),[14f] (*see EMSL basis set library*, *e.g.*, *DZ* (*Dunning*)). Reported here is B98/DZ(2d,p). Full geometry optimizations were performed and uniquely characterized *via* Hessian analysis. Molecular orbital contour plots were generated and depicted using WEBMO,[14g] and QMView:[14h] (*a*) M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su and T. L. Windus, *J. Comput. Chem.*, 1993, **14**, 1347; (*b*) F. A. Hamprecht, A. J. Cohen, D. J. Tozer and N. C. Handy, *J. Chem. Phys.*, 1998, **109**, 6264; (*c*) C. Adamo and V. Barone, *Chem. Phys. Lett.*, 1998, **298**, 113; (*d*) S. Grimme, *J. Comput. Chem.*, 2006, **27**, 1787; (*e*) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; (*f*) T. H. Dunning Jr and P. J. Hay, in *Modern Theoretical Chemistry*, E. H. F. Schaefer III, ed., Plenum, N.Y., 1976, 3; (*g*) T. Cundari, J. R. Schmidt, www.webmo.net; (*h*) K. K. Baldridge and J. P. Greenberg, *J. Mol. Graphics*, 1995, **13**, 63.