

Corannulene Subunit Acts as a Diene in a Cycloaddition Reaction: Synthesis of C₈₀H₃₂ Corannulyne Tetramer

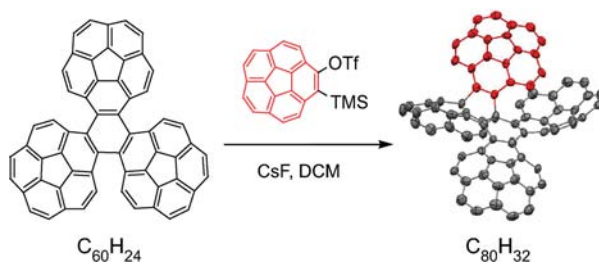
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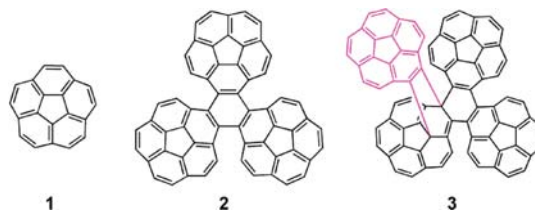
ABSTRACT



Distortion of six-membered rings in corannulene subunits of corannulyne (1,2-didehydrocorannulene) cyclootrimer activates the system for a cycloaddition reaction with another corannulyne unit. This unprecedented cycloaddition in which a corannulene fragment acts as a diene produces the largest oligomer of corannulyne reported to date. X-ray crystallography reveals the highly nonplanar structure of the tetramer which exhibits conformational and optical absorption properties very different from those of the cyclootrimer.

We have been pursuing the development of a practical synthesis of curved-surface polycyclic aromatic hydrocarbons structurally related to the carbon networks of fullerenes (buckybowls).¹ The availability of the smallest buckybowl, corannulene (**1**), on a multigram scale² has allowed for the preparation of several large molecular networks with corannulene subunits.^{1a,b,3} In 2011 we reported a preparation of a C₆₀H₂₄ hydrocarbon (**2**) by palladium catalyzed cyclo-trimerization of corannulyne (1,2-didehydrocorannulene)

generated from *o*-trimethylsilylcorannulenyne triflate.⁴ The highly nonplanar trimer exhibits an interesting conformational behavior with the corannulene subunits, identical in the idealized C₃ symmetry, having dramatically different inversion barriers tuned by the steric congestion. The cyclo-trimer **2** was formed in 40% yield.⁴ More recently we have isolated a minor side product of the reaction accounting for ca. 5% of the products with the molecular formula C₈₀H₃₂ (**3**), as demonstrated by MALDI/TOF.⁵



The structure of **3** could not be elucidated by NMR spectroscopy alone due to the complexity of both ¹H and ¹³C spectra, but it was confirmed by X-ray crystallography

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(1) For recent reviews, see: (a) Sygula, A. *Eur. J. Org. Chem.* **2011**, 1611. (b) Wu, T.-Y.; Siegel, J. S. *Chem. Rev.* **2006**, *106*, 4843. (c) Tsefrikas, V. M.; Scott, L. T. *Chem. Rev.* **2006**, *106*, 4868. (d) Sygula, A., Rabideau, P. W. In *Carbon Rich Compounds*; Haley, M. M., Tykwinski, R. R., Eds.; Wiley-VCH: Weinheim, 2006; p 529.

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(5) See Supporting Information.

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of a single crystal grown from a toluene solution to be a tetramer of corannulyne (Figure 1).⁵

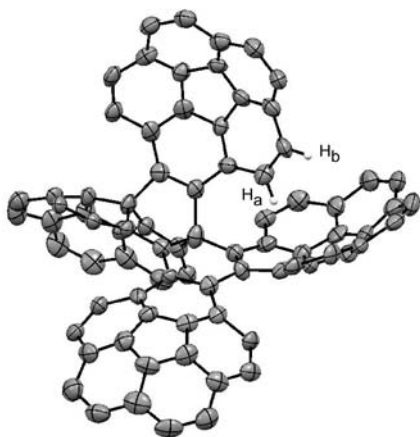
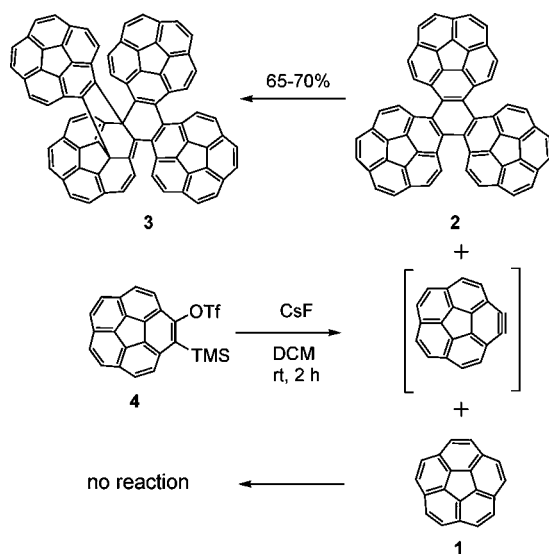


Figure 1. X-ray crystal structure of **3**. The solvating toluene molecules and hydrogen atoms (except for H_a and H_b referred to later) are omitted for clarity.

Clearly, the side product **3** is formed by a cycloaddition of an excess of corannulyne to cyclotrimer **2** formed by cyclotrimerization. The addition of an aryne takes place across one of the six-membered rings of the corannulene subunit adjoining the central ring in **2**.

Indeed, 2 h of treatment of **2** with 1 equiv of *o*-trimethylsilylcorannulenyne triflate (**4**)⁶ with CsF at rt produces

Scheme 1



adduct **3** in 65–70% yield (Scheme 1, top). Considering the high reactivity of arynes in [4 + 2] cycloadditions the formation of **3** may not appear surprising. However, under similar conditions we were not able to detect any detectable

amounts of the expected adducts of corannulyne (or its simpler analog, *o*-benzyne) to corannulene **1** (Scheme 1, bottom). Although the chemistry of corannulene and related buckybowls has recently gained some momentum due to the improved preparative methods for these hydrocarbons, it is usually limited to the functionalization of the rim by substitution reactions.¹ In contrast to fullerenes only a handful of addition reactions to the corannulene C=C bonds have been reported.⁷ In addition, we are not aware of any experimental evidence for corannulene acting as a diene in the Diels–Alder reactions. Computational studies of potential Diels–Alder cycloaddition reactions suggest that corannulene is neither a good dienophile nor diene for these reactions. For example, at the B3LYP/6-31G* level the calculated ΔG_{298}^\ddagger for the model cycloaddition of ethylene to corannulene is higher by ca. 15 kcal mol⁻¹ than that for the unactivated 1,3-butadiene–ethylene pair (51.2 vs 36.4 kcal mol⁻¹, respectively).^{8,9} In line with these findings even very reactive dienophiles like corannulyne or *o*-benzyne fail to generate the cycloaddition products with pristine corannulene (Scheme 1). In this context, formation of **3** provides the first experimental evidence for the corannulene unit acting as a diene in [4 + 2] cycloaddition reactions. Detection of a single regioisomer of cycloadduct **3** indicates that only one of five six-membered rings of corannulene subunits in **2** (i.e., the one adjoining the central ring) is activated enough to react as a diene in the cycloaddition reaction with arynes. Inspection of the crystal structure of trimer **2**⁴ reveals a significant distortion of the rings in question from the optimal geometry of the six-membered rings in pristine corannulene. This includes changes of C–C bond lengths as well as of the torsional angle distortions from the optimal values. As a result, the three six-membered rings are more likely to act as dienes in cycloaddition reactions. Strain-induced activation of benzene rings of cyclophanes toward cycloaddition reactions has been previously reported.¹⁰

Computational studies of the model cycloaddition of the potential dienes **1** and **2** with *o*-benzyne support the above assumptions.¹¹ For the smaller corannulene–*o*-benzyne system we located three distinct transition structures (TSs) for the concerted cycloaddition, resulting from *exo* attack of aryne on corannulene carbon atoms C₁ (rim) and C_{10c} (hub) and both *exo* and *endo* attacks on C_{2a} and C_{10a} carbon atoms.⁵ In accord with the previously reported

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(9) The activation barriers reported in ref 8 are significantly underestimated due to the employment of a small 6-31G* basis set (see Supporting Information).

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(11) HDFT calculations using B3LYP or UB3LYP functionals with 6-31G**, TZVP, and QZVP(-f,-g) basis sets. See Supporting Information for details and references.

computational study of the Diels–Alder cycloaddition of ethylene to **1**,⁸ the *exo* C₁–C_{10c} approach of *o*-benzyne is strongly favored (by ca. 20 kcal mol⁻¹) over the second and third alternative attack. The preferred transition structure for *o*-benzyne to **1** cycloaddition (**TS1**) is shown in Figure 2.

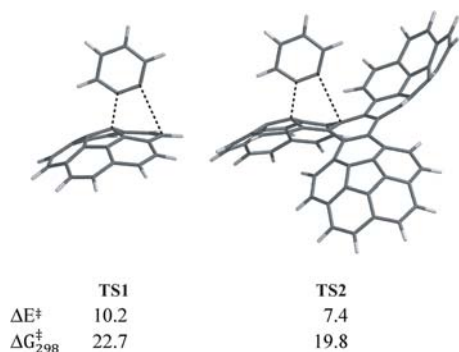
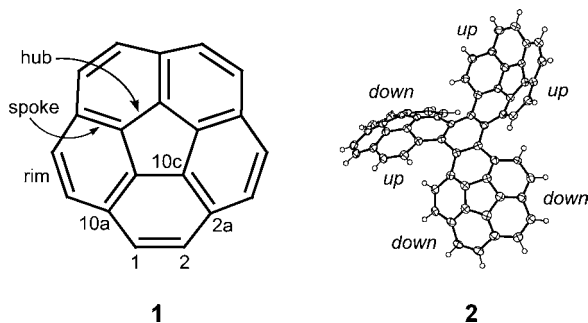


Figure 2. Transition structures for the concerted cycloaddition of *o*-benzyne to **1** and **2** with their uncorrected electronic activation energies (ΔE^\ddagger) and Gibbs free energies (ΔG_{298}^\ddagger , kcal mol⁻¹) calculated at the B3LYP/QZVP* (**TS1**) and B3LYP/QZVP*/B3LYP/TZVP (**TS2**) level.



structural similarities of these transition structures the electronic activation energies (and, subsequently, Gibbs activation free energies) are significantly different. In accord with our experimental findings the activation energy for the cycloaddition of *o*-benzyne with cyclotrimer **2** is ca. 30% lower than that for the reaction with corannulene, indicating a significant activation of the six-membered rings adjacent to the central ring. As expected for cycloaddition reactions, a significant negative ΔS^\ddagger contributes to the free energies of activation in both **TS1** and **TS2** by ca. 12 kcal/mol at 298 K.

Tetramer **3** represents the largest oligomer of corannulyne reported and fully characterized to date. Despite its significant size, **3** is surprisingly well soluble in common organic solvents. Addition of the fourth corannulyne subunit to the trimeric **2** dramatically changes its conformational behavior. While **2** has a broad rt ¹H NMR spectrum which is strongly temperature dependent, **3** exhibits a sharp rt spectrum in which all 32 protons can be identified (Figure 3). Obviously, cycloaddition of the fourth corannulyne to **2** freezes the bowl-to-bowl inversion of the “*up–down*” bowl (the fastest conformational process in **2**)⁴ and modifies the higher energy bowl inversion and flipping dynamics. Interestingly, while 30 of the proton signals are observed in the usual 6.5–8.8 ppm range, two remaining signals (denoted H_a and H_b in Figure 3,

Due to the size and conformational complexity of **2**, only a limited computational study of the cycloaddition of *o*-benzyne to the cyclotrimer was performed. We located a transition structure (**TS2**, Figure 2) assuming a straightforward concerted *exo* attack of *o*-benzyne on the “*up–down*” corannulene subunit in the most stable “*up–down*, *up–up*, *down–down*” conformation of **2** leading to the product with the regio- and stereochemistry analogous to the observed adduct **3**.¹² The calculated electronic activation energies and Gibbs free energies at 298 K are also given in Figure 2.

Both **TS1** and **TS2** exhibit a significant degree of asynchronicity, with the C–C distances from the hub of corannulene to benzyne being much shorter than the analogous distances to the rim. Despite the obvious

Figure 3. ¹H NMR spectrum of **3** (600 MHz, CDCl₃, rt). The proton signals H_a and H_b (shown in the inset) are coupled by ³J = 9.1 Hz.

coupled by a ³J coupling constant of 9.1 Hz) are significantly shifted upfield to 1.78 and 4.36 ppm. GIAO calculations suggest that these signals represent a pair of H-atoms on the fourth corannulene unit located above the concave side of the “*up–up*” bowl (Figure 1).⁵ These protons, strongly magnetically shielded by the “*up–up*” corannulene fragment, are predicted by theory to absorb at 1.46 and 4.34 ppm, in good agreement with the experimental data.^{5,13}

Tetramer **3** exhibits significantly altered photophysical properties as compared to trimer **2**. Both the crystals and solutions of **3** are orange-red while **2** is greenish-yellow.

(12) The potential existence of alternative pathways leading to the *o*-benzyne–**2** adduct through a TS with a lower activation barrier than **TS2** cannot be excluded at this point. Such a pathway would involve an attack of benzyne on one of the remaining two six-membered rings adjoining the central ring in **2** followed by a bowl-to-bowl inversion and/or bowl flipping leading to the most stable conformation.

(13) The upfield ¹H NMR shifts of protons located over the concave faces of the corannulene bowls have been previously reported. For example, see: Seiders, T. J.; Baldrige, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 2754 and ref 3a.

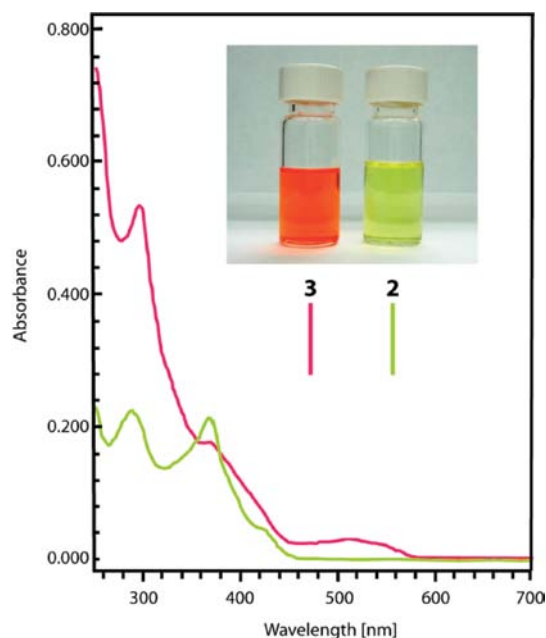


Figure 4. UV/vis absorption spectra of **2** and **3** (1.0×10^{-5} M in DCM).

The UV/vis absorption spectra, shown in Figure 4, reveal that the difference is caused by a very broad and relatively weak absorption band in the range of ca. 460–580 nm in **3**. This spectral feature is apparently missing in **2**. TD B3LYP/6-311G** calculations predict the lowest energy singlet transitions in **2** at 447 and 437 nm with an oscillator strength of 0.01 and 0.09, respectively. These can be related to the shoulder in the UV/vis spectrum found at ca. 425 nm. For **3**, TD calculations predict three lower energy transitions at 588, 498, and 470 nm with the major contributions from HOMO to LUMO, HOMO–1 to LUMO, and HOMO to LUMO+1 excitations, respectively. Extension of π -conjugated systems usually result in a narrowing of their HOMO–LUMO gaps, but in the case of **3** we did not expect any significant buildup of π -conjugation in comparison to trimer **2** since the incoming “fourth” corannulene subunit is bound to the rest of the

molecule through the formally sp^3 hybridized carbon atoms and the resulting structure is highly nonplanar, thus minimizing the long-distance conjugation. Nevertheless, DFT calculations find that the HOMO–LUMO gap in **3** is significantly narrower than in **2** (2.56 vs 3.32 eV), a result of both the higher HOMO and lower LUMO energies in **3** (by 0.46 and 0.30 eV, respectively).⁵ Thus, the reduced HOMO–LUMO gap in **3** explains the change in its light absorption properties.

In conclusion, we report the first cycloaddition of a dienophile to the corannulene subunit acting as a diene. As confirmed by HDFT calculations, distortion of six-membered rings adjacent to the central ring in cyclootrimer **2** significantly lowers the electronic activation energy of the reaction as compared to the pristine corannulene. The resulting highly nonplanar hydrocarbon $C_{80}H_{32}$ (**3**) representing the largest oligomer of corannulene reported to date exhibits conformational and photophysical behavior quite different from that of the smaller corannulyne cyclootrimer **2**. The diene-like behavior of corannulene fragments in sterically hindered systems such as **2** presents new opportunities to generate large, highly nonplanar carbon-rich molecular architectures with interesting and potentially useful steric and electronic properties.

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Supporting Information Available. Experimental details; 1H , ^{13}C , and COSY NMR spectra of **3**; computational results including geometries of the located transition structures with their activation barriers; HOMO–LUMO contours of **2** and **3**; GIAO calculated chemical shifts for **3**; CIF file for **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

The authors declare no competing financial interest.