Organic LETTERS

Letter

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Bis-corannulenoanthracene: An Angularly Fused Pentacene as a Precursor for Barrelene-Tethered Receptors for Fullerenes

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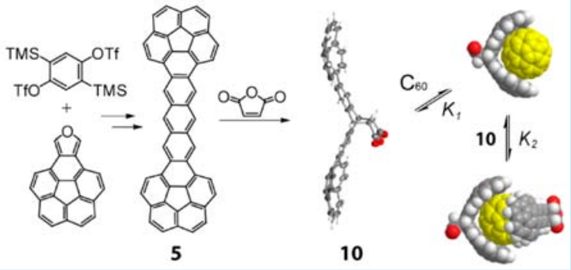
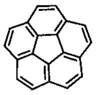
Ⓢ *Supporting Information*

ABSTRACT: Bis-corannulenoanthracene ($C_{50}H_{22}$, **5**) was prepared by the Diels–Alder double cycloaddition of isocorannulenofuran with "bis-benzyne", followed by deoxygenation of the adducts. Despite the presence of a pentacene core, **5** is stable enough to be isolated and stored. A cycloaddition reaction of **5** with maleic anhydride produces **10** which exhibits strong affinity toward C_{60}, as evidenced by ^1H NMR titration experiment. Synthesis of **10** demonstrates the synthetic utility of hydrocarbon **5** in the preparation of the barrelene-based molecular clips with two benzocorannulene pincers adorned with polar substituents on their tethers, which will allow for immobilization of the receptors on solid supports.



We have been pursuing a development of the efficient molecular receptors for fullerenes based on the paradigm of size/shape complementarity of the convex surfaces of these carbon cages with the accessible concave faces of buckybowls.[1] The dispersion forces binding the most popular fullerene C_{60} with the smallest buckybowl, corannulene (**1**), although predicted to be quite substantial in the gas-phase, are not strong enough to overcome the usual solvation and entropy penalties associated with the supramolecular assembly formation in solution.[2] However, we have demonstrated that very efficient molecular clips with two benzocorannulene pincers can be constructed if the pincers are preorganized on a proper tether. Such receptors (e.g **2**, **3**, and **4**) with, respectively, dibenzocyclooctatetraene,[3] norbornadiene,[4] and one of the Klärner's tethers[5] exhibit high association constants with both C_{60} and C_{70} in toluene and in chlorobenzene. In addition, X-ray crystal structure determination of the supramolecular inclusion complexes of fullerenes with these receptors provides the evidence for the "ball-in-socket" arrangement of the carbon cages encapsulated by both benzocorannulene pincers. The optimal receptor's topology, maximizing the host–guest concave–convex dispersion interactions, has also been rationalized by computational studies.[3−6] Following the report of the original "buckycatcher", other bis- and tris-corannulene receptors for fullerenes have also been reported by us and others.[7]

For some time we have considered a preparation of the $C_{50}H_{22}$ hydrocarbon (**5**) as a precursor for a series of receptors with two benzocorannulene pincers preorganized on barrelene tethers if **5** can be employed as a diene in the Diels–Alder cycloaddition reactions. Taking into account the well-known stability limits of larger linear acenes (starting with pentacene),[8] the question arises whether **5**, formally possessing a pentacene core, would be stable enough to be isolated. However, the previously reported fused tetrabenzopentacene (**6**) was found to be "considerably less reactive than pentacene, but it still reacted readily with maleic anhydride to form a cycloadduct".[9] We therefore assessed the potential reactivity/stability of **5** in comparison to pentacene and tetrabenzopentacene (**6**) by calculating the HOMO–LUMO gaps for the three hydrocarbons. At the B3LYP/6-311G(d,p) level the calculated gap for **5** is 2.65 eV, virtually identical with the one calculated for Clar's tetrabenzopentacene (2.64 eV). Both these numbers are significantly higher than the 2.20 eV HOMO–LUMO gap calculated for the parent pentacene, indicating that the anticipated stability of **5** should be similar to that of **6** rather than pentacene. Herein we report the synthesis of the novel bis-corannulene hydrocarbon **5** (which, like its smaller analogue **6**, is stable enough to be isolated) and demonstrate its potential for the preparation of barrelene-based molecular receptors for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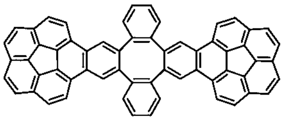
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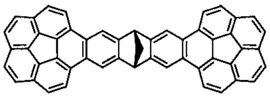
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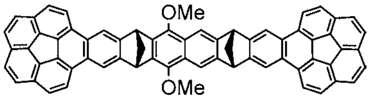

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Received: April 11, 2016
Published: June 9, 2016

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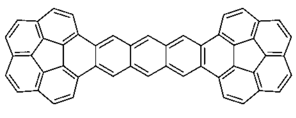
DOI: 10.1021/acs.orglett.6b01049
Org. Lett. 2016, 18, 3054−3057

fullerenes with two benzocorannulene pincers by the Diels–Alder cycloaddition reaction with maleic anhydride.



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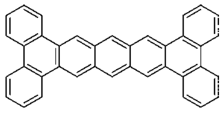

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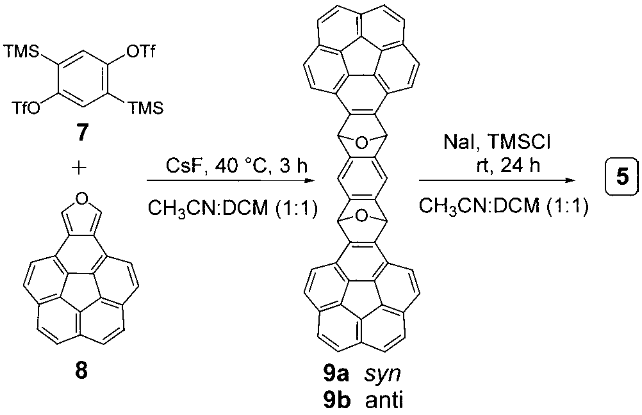
Clar's preparation of tetrabenzopentacene **6** started with the Friedel–Crafts acylation of octahydrophenathrene with pyromellitic anhydride.[9] In our hands, however, acylation of corannulene with the same anhydride led to the extremely insoluble products, presumably polyquinones, resisting further reduction to the expected hydrocarbons. We therefore switched to benzyne chemistry. The synthesis of **5** is shown in Scheme 1.

Scheme 1. Synthesis of $C_{50}H_{22}$ Hydrocarbon 5



Bis-benzyne precursor **7**, prepared by a slightly modified Wudl's procedure,[10] was employed along with the reactive diene **8**, introduced by our group some time ago.[11] Thus, one-pot double cycloaddition of **8** to the bis-benzyne, formed sequentially by the action of CsF on the precursor **7**, produced a mixture of two isomeric endoxides **9a** and **9b** (ca. 5:3) in a combined yield of 61%. The separation of the stereoisomers, while unnecessary for the synthesis of **5**, was easily achieved due to the significantly different solubilities of the two in dichloromethane (DCM). Both isomers were separately characterized by MS as well as by ^{1}H and ^{13}C NMR spectroscopy.[12] In addition, X-ray crystal structure determination of the less soluble adduct **9b** provided the proof for its *anti* configuration (Figure 1).[12,13]

Deoxygenation of both **9a** and **9b** was achieved by *in situ* generated trimethylsilyl iodide to yield **5** as a bright red solid.

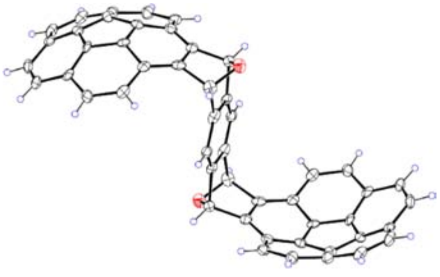


Figure 1. Crystal structure of *anti* endoxide **9b** with 50% ellipsoids. The molecule lies on an inversion center in the crystal.

Not surprisingly, **5** is only sparingly soluble in organic solvents which prevented its characterization by NMR spectroscopy. On the other hand, UV–vis absorption and fluorescence spectra of **5** in 1,2,4-trichlorobenzene (TCB) were recorded and compared to the spectra of tetrabenzopentacene **6**, prepared from **7** and phenanthrenefuran by the procedure presented in Scheme 1. Both hydrocarbons exhibit very similar spectral patterns with the absorption and emission spectra of **5** displaying a slight red shift as compared to the smaller analogue **6** (Figure 2). The longest wavelength absorptions λ_{max} for **5** and **6** (510 and 504 nm, respectively) are a considerably shorter wavelength than in the case of pentacene (582–585 nm),[8,10] indicating the smaller HOMO–LUMO gap in the latter. Both **5** and **6** are strongly fluorescent and exhibit small Stokes shifts of 6 and 3 nm, respectively.

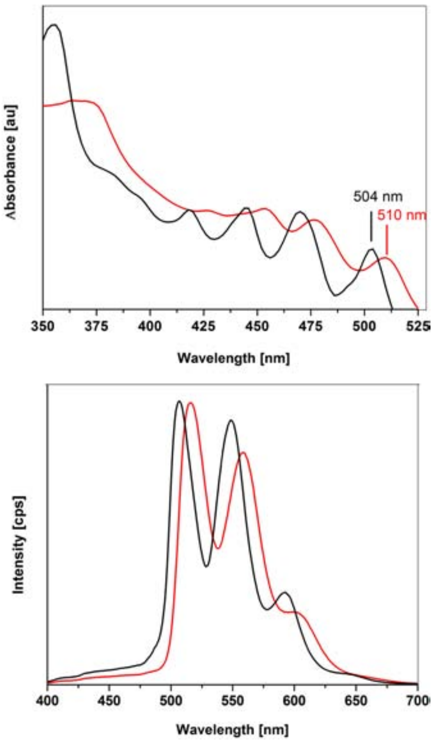


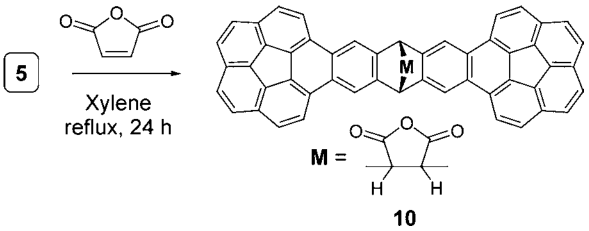
Figure 2. UV–vis absorption spectra (top) and emission spectra (bottom) of **5** (red) and of **6** (black) in TCB.

As mentioned above, the calculated HOMO–LUMO gaps for **5** and **6** are virtually identical (2.65 and 2.64 eV) and significantly larger than in the case of pristine pentacene (2.20 eV), in accord with the observed highest reactivity of the latter. On the other hand, an assessment of the aromatic character of the three hydrocarbons on the basis of the nucleus-independent chemical shifts (NICS)[15a] calculated with PBE1PBE/6-311+G** on B3LYP/TZVP geometries indicates that the central rings in **5** and **6** with NICS(1) values of −12.9 and −12.7 are slightly less aromatic than in the case of pentacene (NICS(1) = −14.1), contradicting the experimentally established relative stabilities of these hydrocarbons. In addition, in all three cases the diatropic ring currents are greater than in benzene itself (NICS(1) = −10.4). Apparently, as previously reported, the differences in reactivity of polyacenes depend on the change of aromaticity during the reaction rather than on the aromaticities of the substrates.[15b,c]

DOI: 10.1021/acs.orglett.6b01049
Org. Lett. 2016, 18, 3054–3057

In analogy to tetrabenzopentacene **6**,[9] **5** undegoes the Diels−Alder cycloaddition with maleic anhydride producing bis-benzocorannulene receptor **10** in a moderate yield of 52% (Scheme 2). The bowl-shaped topology of the corannulene subunits along with their low bowl-to-bowl inversion barriers gives rise to four distinct conformations **10a**−**10d**. In the gas phase all conformers are calculated to be virtually isoenergetic (within 0.4 kcal/mol).[12] X-ray crystal structure determination of the crystal grown from a toluene−DCM solution of **10** shows that the bis-convex conformation of the receptor (**10d**) is preferred for the toluene solvate in the solid state (Figure 3)[12,16] A similar conformational preference was previously observed in the crystal of DCM solvate of a smaller dicorannulenobarrelene analog **11** which did not exhibit measurable association with C_{60} in toluene.[17]

Scheme 2. Synthesis of the Molecular Receptor 10



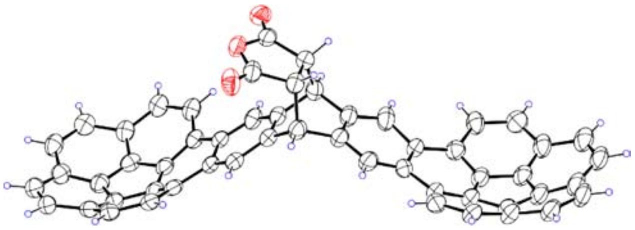
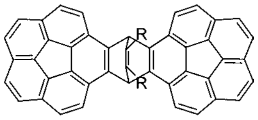


Figure 3. Crystal structure of the toluene solvate of **10** with 50% ellipsoids. The molecule is disordered by tilting with respect to a mirror plane across which it lies. The disorder and the solvating toluene molecule are not shown.

10a **10b** **10c** **10d**



11: R = COOMe

Clearly, bis-concave conformation **10a** is of special interest if its potential as the receptor for fullerenes is considered, since it would employ both concave surfaces of the corannulene pincers to accommodate the guest carbon cage. Since the bowl-to-bowl inversion barriers for corannulenes are quite low and the calculated gas-phase energy of **10a** is only 0.27 kcal/mol higher than that of **10d** (observed in the crystal) or 0.36 kcal/mol higher than the lowest energy, **10c**,[12] it is expected that the bis-concave conformation could be preferred in the supramolecular assemblies of **10** with fullerenes. The gas-phase binding energy of **10** with C_{60} calculated with B97-D/QZVP′ is virtually identical with the original buckycatcher (**2**) and only slightly lower than calculated for the more efficient receptor **3**, predicting the strong affinity of **10** toward fullerenes (Table 1).

Table 1. Comparison of Binding Properties of Buckycatchers 2, 3, and 10

	BE[a]	K_1[b]	K_2[b]
2	41.8	520 ± 20[c]	not detected
3	42.5	10 040 ± 110[d]	1180 ± 640[d]
10	41.7	3610 ± 20	2000 ± 120

[a] Gas-phase binding energies [kcal mol^{-1}] calculated at B97-D/QZVP′//B97-D/TZVP level. [b] [M^{-1}] in PhCl-d_5. [c] Reference 4. [d] Reference 5.

Indeed, a ^{1}H NMR titration experiment demonstrates the formation of the inclusion complexes of C_{60} with **10** in PhCl-d_5 as evidenced by the chemical shift changes of the receptor's hydrogen atoms induced by the changes in C_{60} concentrations. The continuous variation (Job) plots derived from the titration data have their maxima at ca. 0.5 molar fractions of the receptor, indicating the predominance of the 1:1 stoichiometry of the binding event. On the other hand, some dissymmetry of these curves is observed at the receptor molar fractions higher than 0.5 which can be attributed to minor contributions from the trimeric $C_{60}@\mathbf{10}_2$ complex formation (eq 1).[12] It should be pointed out that the previously

$$\mathbf{10} + C_{60} \overset{K_1}{\rightleftharpoons} C_{60}@\mathbf{10} + \mathbf{10} \overset{K_2}{\rightleftharpoons} C_{60}@\mathbf{10}_2 \qquad (1)$$

studied buckycatchers **2** and **3** exhibited different modes of association with fullerenes in chlorobenzene with the more efficient receptor **3** forming both 1:1 and 2:1 supramolecular assemblies[4] while only 1:1 associates of buckycatcher **2** with C_{60} were detected in solution and in the solid state.[3] Receptor **10** seems to represent a borderline case between **2** and **3**. Thus, nonlinear fitting of the titration data was attempted with both 1:1 and the stepwise 2:1 stoichiometric models, and the results were tested using F-statistics. As expected, fitting of the experimental results with the four-parameter 2:1 stoichiometry model is better than the one obtained with the two-parameter 1:1 model. In addition, F-testing indicates that the fitting improvement of the experimental data with the 2:1 stoichiometric model is statistically significant.[12] The association constants were therefore estimated with this model, and they are shown in Table 1. Apparently, **10** exhibits strong affinity toward C_{60}, significantly higher than the dibenzocyclooctatetraene-based buckycatcher **2**, even though the gas-phase calculated binding energies for both buckycatchers are virtually identical (Table 1). The higher K_1 for **10** in comparison with **2** means that the Gibbs free energy of the 1:1 complexation of the former catcher with C_{60} in PhCl at rt is more exergonic by ca. 1.1 kcal/mol. In addition, in contrast with **2**, the formation of the trimeric $C_{60}@\mathbf{10}_2$ assembly is significant under the conditions of the NMR titration experiment. On the other hand, **10** is not as efficient a molecular trap for C_{60} as the norbornadiene-tethered buckycatcher **3**, with its estimated free energy of the 1:1 inclusion complex formation being less exergonic by ca. 0.6 kcal/mol.

In conclusion, bis-corannulenoanthracene **5** prepared by the Diels−Alder cycloaddition of a "bis-benzyne" with isocorannulenofuran **8** is stable enough to be isolated and stored, despite the presence of a pentacene subunit in its core. On the other hand, **5** acts as a reactive diene and adds proper dienophiles by a cycloaddition with its central benzene ring, as demonstrated by the reaction with maleic anhydride. The resulting substituted barrelene **10** exhibits two benzocorannulene pincers properly preorganized to adopt a fullerene cage. The ^{1}H NMR titration experiment proves the high affinity of **10** toward C_{60}. Availability of **5** allows for the preparation of a series of the barrelene-based bis-benzocorannulene receptors with polar groups on their tethers which, in addition to the potential to act as the efficient molecular receptors for fullerenes, will allow for their deposition on solid supports. We are currently exploring these possibilities.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b01049.

> Synthetic procedures, NMR and MS spectra for **5**, **9**, and **10**; ^{1}H NMR titration studies; DFT calculations four conformers **10a–10d** and for the inclusion complex C_{60}@**10**; X-ray data for the toluene solvates of **9b** and **10** (PDF)
>
> Crystallographic data for the toluene solvates of **9b** and **10** (CIF, CIF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support of this work from the Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy through Grant DE-FG02-04ER15514 and from the Department of Chemistry, Mississippi State University, is gratefully acknowledged by A.S.

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(2) A low association constant of 19 M^{-1} was determined for the cationic endohedral complex $Li^+@C_{60}@$**1** in PhCN at rt, while the association constant for the pristine corannulene with C_{60} formation under the same conditions was estimated to be $\ll 1$ M^{-1}. Yamada, M.; Okhubo, K.; Shionoya, M.; Fukuzumi, S. *J. Am. Chem. Soc.* **2014**, *136*, 13240–13248.

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(12) See the Supporting Information.

(13) **9b** as the toluene solvate. X-ray data were collected at $T = 101$ K with Cu Kα radiation on a Bruker Kappa APEX-II DUO diffractometer to $\theta_{max} = 72.3°$, yielding 3994 independent reflections. Crystal data monoclinic $P2_1/n$, $a = 11.0215(5)$ Å, $b = 13.1109(6)$ Å, $c = 15.1972(7)$ Å, $\beta = 111.193(2)°$, $Z = 2$, $R = 0.1111$, and 3704 refined parameters. Disordered solvent contribution was removed using the SQUEEZE procedure, amounting to about 2.8 molecules of toluene per molecule of **9b**.[14] Crystallographic results can be obtained as deposition no. CCDC 1462819 from the Cambridge Crystallographic Data Centre. A CIF is also available as Supporting Information.

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(16) **10** as the toluene solvate. X-ray data were collected at $T = 90$ K with Cu Kα radiation on a Bruker Kappa APEX-II DUO diffractometer to $\theta_{max} = 62.3°$, yielding 3116 independent reflections. Crystal data monoclinic $P2_1/m$, $a = 10.8890(4)$ Å, $b = 13.3104(6)$ Å, $c = 13.9583(6)$Å, $\beta = 106.526(2)$, $Z = 2$, $R = 0.046$, 538 refined parameters, and 530 restraints. The main molecule lies across a mirror plane and is disordered by a tilt of approximately 11° from the mirror. The anhydride C_2O_3 moiety is further disordered into two orientations with a 71:29 relative population. The toluene molecule is also disordered. Crystallographic results can be obtained as deposition no. CCDC 1473172 from the Cambridge Crystallographic Data Centre. A CIF is also available as Supporting Information.

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