

Synthesis and Columnar Organization of Partially Fluorinated Dehydrobenz[18]annulenes

Sumitra Karki, Lucas J. Karas, Xiqu Wang, Judy I. Wu,* and Ognjen Š. Miljanić*



ABSTRACT: Two diamond-shaped and partially fluorinated dehydrobenz[18] annulene macrocycles have been prepared through a one-pot synthesis relying on four-fold Sonogashira coupling. Single-crystal structures of these macrocycles show continuous columnar stacks held together by the fluoroarene–alkyne, arene–alkyne, fluoroarene–fluoroarene, and alkyne–alkyne [$\pi \cdots \pi$] interactions instead of the expected fluoroarene–arene [$\pi \cdots \pi$] interactions.

hape-persistent dehydrobenzannulenes (DBAs; also Known as arylene ethynylene macrocycles, AEMs) of various geometries and sizes have been pursued as synthetic targets for more than half a century.¹⁻⁶ These π -conjugated macrocycles with conformationally rigid backbones and central cavities have been used in supramolecular chemistry and molecular recognition,^{7–11} host–guest chemistry,¹² as components of organic sensors¹³ and organogels,¹⁴ nanoporous solids, and liquid crystals.^{15–21} Moore and co-workers' report that these macrocycles can form dimers and higher aggregates through $[\pi \cdots \pi]$ interactions between the aromatic rings^{22,23} started attempts to modulate this aggregation by the installation of electron-donating,²⁴ electron-withdrawing,²⁵ or hydrogen bonding²⁶ units onto the DBAs. As benzene and hexafluorobenzene $[\pi \cdots \pi]$ stack in an electronically complementary and well-ordered alternating arrangement-a fact first recognized by Patrick and Prosser in 1960²⁷ and since studied in great detail²⁸⁻³⁰—we speculated that their joint incorporation into the DBA structures could result in the formation of higher-order columnar assemblies in the solid state.

Given their interest to supramolecular chemistry,^{31–36} several partially and fully fluorinated DBAs have been synthesized, and their aggregation behavior has been studied through concentration-dependent NMR and UV–vis spectroscopy, vapor pressure osmometry (VPO), and single-crystal X-ray diffraction (XRD).^{26,37,38} Shu and co-workers have shown that the favored fluoroarene–arene interactions lead to

the aggregation of a hexagonally shaped, partially fluorinated diyne-linked DBAs, as evidenced by the SEM images which showed the formation of rod-like crystallites with a hexagonal cross-section.³⁹ However, most of these studies were performed on the six- or three-fold symmetric DBAs, in which the arene and the fluoroarene components shared either an *ortho*³⁷ or a *meta*^{38,39} substitution pattern. In this Communication, we present the synthesis and crystallographic characterization of two diamond-shaped partially fluorinated DBAs 1 and 2 (Scheme 1). These two macrocycles have two *meta*-connected arene and two *ortho*-connected tetrafluoroarene rings bridged by ethynylene moieties. Macrocycle 2 was synthesized to examine the influence of the exoannular substitution on the packing of the diamond-shaped macrocycle.

One-pot syntheses of macrocycles 1 and 2 (Scheme 1) were accomplished by reacting the commercially available 1,2diiodo-3,4,5,6-tetrafluorobenzene (3) with diynes 4^{40} and 5,^{41,42} which themselves were prepared following literature

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Scheme 1. Syntheses of Dehydrobenz[18]annulene Macrocycles 1 and 2 via Sonogashira Coupling



Figure 1. (A) Crystal structure of macrocycle 1. Its extended packing diagram (B) shows slipped columnar stacking of molecules of 1 (C), mediated by T-shaped fluoroarene-fluoroarene interactions (D) and fluoroarene-alkyne $[\pi \cdots \pi]$ interactions (E).



Figure 2. (A) Crystal structure of macrocycle 2. Its extended packing diagram (B) shows slipped columnar stacking of molecules of 2 (C), mediated by T-shaped interactions (D), as well as a combination of hydrogen bonding, fluoroarene-fluoroarene, and alkyne-alkyne $[\pi \cdots \pi]$ interactions (E).

procedures. Macrocycle 1 was isolated as a brown solid in 22% yield after successive recrystallizations from PhMe/Me₂CO and PhMe/MeCN solvent systems. Macrocycle 2 was obtained after column chromatography eluting with DCM/hexanes as a white solid in 5% yield. Their relatively low yields were caused by the presence of side products, which were either linear uncyclized oligomers or the reduced unreactive materials in which the aryl-appended iodine atom was replaced with a hydrogen. The yield of 2 was presumably further eroded by the lowered reactivity of electron-poor alkyne 5 relative to 4. Nevertheless, one-step syntheses allowed the preparation of sufficient amounts of 1 and 2.

To study the packing behavior of 1 and 2, we grew single crystals of both macrocycles. Diffraction-quality needle-shaped single crystals of 1 were produced by allowing the solution of 1 in hot N,N-diethylacetamide (DEA) to first slowly cool down to room temperature and then evaporate over 2 days. Rod-shaped single crystals of 2 were obtained from its hot solution of THF, which was first slowly cooled to room temperature and then left to evaporate over 2 days.

Macrocycle 1 crystallizes in the $P2_1/n$ space group with two molecules per unit cell. As shown in Figure 1A, it is only slightly distorted from planarity, with the dihedral angle between the planes of fluorinated and nonfluorinated rings of



Figure 3. Comparison of the interaction patterns between the DBA macrocycles 6 (A),²¹ 1 (B), and 2 (C).



Figure 4. (A–C) Selected structures from the CSD showing examples of fluoroarene–alkyne $[\pi \cdots \pi]$ interactions.^{45–47}

9.58°, and the distance between two intraannular hydrogens of 2.42(3) Å. The extended packing diagram (Figure 1B) shows that the macrocycles organize into columnar stacks through slipped parallel stacking shown in Figure 1C. The closest points of contact between these stacks are observed in [C-H… F] distances of 2.56 (5) Å between orthogonal stacks and $[F \cdots$ F] contacts between parallel columns at 2.63(4) Å. Closer inspection of the packing shows that the crystal structure is held together by the T-shaped fluoroarene-fluoroarene interactions between the macrocycles of 1 with a 2.91(3) Å short contact between a fluorine and a carbon atom (Figure 1D). The interactions between the neighboring macrocycles within the stack are not the expected fluoroarene-arene interactions but instead the apparent fluoroarene-alkyne $[\pi \cdots \pi]$ interactions highlighted in Figure 1E. Two macrocycles arrange in a slipped stacking interaction in a way where two of the carbon atoms of the fluoroarene reside above the alkyne with a centroid-centroid distance of 3.29(3) Å and two additional short arene-alkyne contacts of 3.37(3) Å; both are shorter than the sum of the van der Waals radii of two carbon atoms (3.40 Å).

Macrocycle 2 (Figure 2A) crystallizes in the $P2_1/c$ space group with two molecules per unit cell. The dihedral angle between the planes of fluorinated and nonfluorinated rings is again very small (5.84°), and the distance between the intraannular hydrogen atoms is 2.43(3) Å. As seen in macrocycle 1, macrocycle 2 also forms a continuous columnar stack (Figure 2B) with slipped stacking between the macrocycles (Figure 2C) and T-shaped interactions (Figure 2D). However, their closer inspection reveals an interaction different from that observed in 1: the molecules of 2 are not stacking via the fluoroarene–alkyne interactions (Figure 2E). The two macrocycles are slipped in a way that results in the shortest contacts of 3.22(2) Å between the carbons of the fluoroarenes, and 3.32(2) Å between the carbons of alkynes. The third interaction between the two molecules of macrocycle 2 is evidenced by a short contact of 2.71(2) Å between the oxygen and hydrogen of the methyl group. This tentative $[C-H\cdots O]$ hydrogen bond thus appears to play an important role in modulating the slipped stacking of molecules of 2. The closest intercolumn contact is seen at an $[F\cdots F]$ distance of 2.74(4) Å; importantly, the $[C-H\cdots F]$ short contacts observed in the structure of 1 are not seen for 2, presumably on account of the steric hindrance of the ester group.

The nonfluorinated analogue of 1, dehydrobenz[18]annulene 6, was previously synthesized.^{43,44} While the two compounds and the esterified analog 2 have very similar molecular structures, their packing arrangements differ quite profoundly. The crystal structure of 6 is held together by four T-shaped arene interactions between a hydrogen and a carbon of another arene (Figure 3A) with only a short contact of 2.87(3) Å, whereas the fluorinated analogues 1 and 2 form slipped parallel stacks via fluoroarene–alkyne and arene– alkyne [$\pi \cdots \pi$] interactions in the case of 1 (Figure 3B), and hydrogen bonding, fluoroarene–fluoroarene, and alkyne– alkyne [$\pi \cdots \pi$] interactions in the case of 2 (Figure 3C). The fluorination thus plays a critical role in forcing the columnar assembly of macrocycles 1 and 2.

Intrigued by the observation of fluoroarene–alkyne short contacts instead of the expected fluoroarene–arene $[\pi \cdots \pi]$ interactions in the case of 1, we searched for other examples of fluoroarene–alkyne interactions in the Cambridge Structural Database (CSD). Figure 4 shows several examples. In the cocrystal of octafluoronaphthalene and diphenylacetylene (Figure 4A), alternate stacks form between two molecules via the fluoroarene–alkyne interactions with short contacts of 3.32(2) Å.⁴⁵ Similarly, as shown in Figure 4B, the structure of the cocrystal of 4,4-diphenylethynyl-2,2-bipyridine with hexafluorobenzene also shows that the fluoroarene is not

4C also shows continuous stacking led by the π -interaction between a fluoroarene and an alkyne instead of the fluoroarene–arene interactions.⁴⁷ Several additional examples show fluoroarene–alkyne interactions despite the presence of an arene moiety available for a possible fluoroarene–arene interaction (see Figure S11A–D).^{48–52} This situation is observed in organic compounds, as well as in some of the metal complexes, although not many studies aimed to explain the observed patterns (see Figure S11E–I).^{53–57}

The preference for the fluoroarene–alkyne interaction over the fluoroarene–arene interaction has also been observed in macrocyclic structures. For example, Bunz and co-workers observed that the cocrystal of hexafluorobenzene and the cyclic dimer of *ortho*-diethynylbenzene shows a stacking pattern in which hexafluorobenzene centers above the alkyne moieties rather than the benzene rings of the macrocycle.⁵⁸ Tahara and co-workers have synthesized the functionalized triangular dehydrobenzo[12]-annulenes and observed that the fully fluorinated macrocycle stacks via fluoroarene–alkyne interactions. The same fluorinated DBA showed the fluoroarene– arene interaction when cocrystallized with the triply *N*,*N*dimethylamino-substituted dehydrobenz[12]-annulene.⁵⁹

Moore and co-workers have concluded that the π interactions between arenes and alkynes are not significantly stabilizing in DBAs.²² However, fluorinating the arene may change this conclusion; the above-mentioned linear synthons, macrocycles, and our macrocycle 1 show that the fluoroarenes often engage in $[\pi \cdots \pi]$ interactions with the alkyne moieties even in the presence of arenes within the molecule available for a potential fluoroarene—arene interaction.

Density functional theory (DFT) computations were performed for dimers of the macrocycles 1 and 2 to understand factors relevant for their self-association. Both 1 $(-31.4 \text{ kcal mol}^{-1})$ and 2 $(-39.6 \text{ kcal mol}^{-1})$ exhibit large negative dimerization energies, suggesting strong interactions between the macrocycles. All computations were performed at the B3LYP-D3/6-311+G(d,p)//B3LYP-D3/6-31+G(d) level of theory, employing Gaussian 16.60 The interaction energy for the dimer of 1 may be attributed to multiple π -interactions between the triple bonds and the arene rings. It is interesting to note that in the optimized geometry for alkyne-arene π interactions, the alkyne normally resides over the center of the arene ring, but in the fluorinated macrocycle 1 the alkyne moieties reside over the edge of the fluoroarene rings. We hypothesize that this slipped packing helps maximize the number of $[\pi \cdots \pi]$ and electrostatic interactions (see computed electrostatic potential map, Figure S9). The stronger interaction energy in the dimer of macrocycle 2 shows that hydrogen bonding plays an important role in stabilizing the packing arrangement. In fact, the computed interaction energy of macrocycle 2 is very close to that reported by Zhong et al. for stacked hexameric macrocycles with multiple hydrogen bonding interactions that drive the dimer formation.²⁶ Thus, hydrogen bonding can be seen as a decisive factor that differentiates the packing behavior of the macrocycles 2 and 1.

In summary, we prepared two partially fluorinated dehydrobenz[18]annules 1 and 2 via a one-pot route. Their single-crystal structures show that the two macrocycles organize into columnar stacks, which are critically enabled by the presence of the fluorinated rings. In macrocycle 1, those rings engage in apparent $[\pi \cdots \pi]$ stacking fluoroarene-alkyne

interactions. While the fluoroarene–arene interaction was found to direct the columnar stacks in the most symmetric hexameric macrocycles, in the case of diamond-shaped macrocycles with ortho- and meta-linked fluoroarene and arene groups, columnar stacking has been achieved via fluoroarene–alkyne interaction. Our ongoing work aims to explore the generality of this assembly pattern and its relevance in the construction of advanced materials.⁶¹

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.cgd.2c00178.

Experimental procedures, copies of NMR spectra, spectroscopic analysis, and computational analysis at B3LYP-D3/6-31+G(d) (PDF)

Accession Codes

CCDC 2109154–2109155 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Authors

- Ognjen Š. Miljanić Department of Chemistry, University of Houston, Houston, Texas 77204-5003, United States; orcid.org/0000-0002-7876-9034; Email: miljanic@ uh.edu
- Judy I. Wu Department of Chemistry, University of Houston, Houston, Texas 77204-5003, United States; Occid.org/ 0000-0003-0590-5290; Email: judyicwu@gmail.com

Authors

- Sumitra Karki Department of Chemistry, University of Houston, Houston, Texas 77204-5003, United States; orcid.org/0000-0002-1062-3573
- Lucas J. Karas Department of Chemistry, University of Houston, Houston, Texas 77204-5003, United States; orcid.org/0000-0001-7970-119X
- Xiqu Wang Department of Chemistry, University of Houston, Houston, Texas 77204-5003, United States

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.cgd.2c00178

Author Contributions

S.K. prepared and crystallized 1 and 2. X.W. solved their crystal structures. L.J.K. performed the computations with insights from J.I.W. S.K. and O.Š.M. wrote the manuscript, incorporating comments from all other authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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