

# Construction of Multiple Five-Membered Rings in Dibenzo[*g*,*p*]chrysene Core for the Synthesis of a Nona-Cycle Buckybowl

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 $C_{60}$ -fragmentary bowl-shaped molecules, commonly referred to as "buckybowls", are provocative compounds, and their inviting functions based on the non-planar  $\pi$ -conjugation are expected. Yet, achieving synthesis of some kinds of the curved structure remaining challenging. Herein we report skeletal construction of a nona-cyclic buckybowl that is synthetically unachievable heretofore, namely, 3,10-dihydroindeno[7,1,2-pqr]-as-

#### Introduction

Buckminsterfullerene (C<sub>60</sub>) is a historical, monumental, and seminal molecule in multiple chemical areas. Its gently curved architecture has fascinated chemists since it was reported in 1985.<sup>[1]</sup> C<sub>60</sub>-fragmentary bowl-shaped substructures are also appealing compounds that are commonly referred to as "buckybowls."<sup>[2]</sup> Buckybowls contain some pentagonal rings right beside hexagonal ones; for example, hexa-cycle corannulene (C<sub>20</sub>H<sub>10</sub>) and hepta-cycle sumanene (C<sub>21</sub>H<sub>12</sub>) are representative of buckybowls.<sup>[3,4]</sup> Other larger-sized buckybowls are known to be namely deca-cycle hemifullerene (C<sub>30</sub>H<sub>12</sub>) and trideca-cycle circumtrindene (C<sub>36</sub>H<sub>12</sub>).<sup>[5–7]</sup>

From the synthetic point of view, two types of protocols lead to those geodesic polyarenes: One is flash vacuum pyrolysis (FVP), and the other is non-pyrolytic strategies.<sup>[8]</sup> If the precursors of such polyarene are nearly insoluble, FVP method is occasionally effective for forming desired curvatures at once.<sup>[9,10]</sup> The major shortcomings of FVP are harsh conditions that limit bonding with substituents and refining products and enhancing productivity. Alternatively, non-pyrolytic strategies have benefited scale-up and purification of products particularly when the strategies are bottom-up syntheses in solution phase.<sup>[11,12]</sup> Solution-phase synthesis sometimes requires com-

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indaceno[3,2,1,8,7-*defghi*]chrysene. The key to success was solution-compatible process in which a multiple substituted dibenzo[*g*,*p*]chrysene is amenable to threefold formation of five-membered rings at its periphery. The resulting scheme here, coupled with the gently curved scaffold, offers a new insight into the solution-phase synthesis of curved and twisted polyarenes.

plex building blocks and laborious multiple steps, whereas it allows scalable production and selective transformation and ingenious manipulation.<sup>[13,14]</sup>

Herein we present solution-phase synthesis of a nona-cyclic buckybowl frame, namely 3,10-dihydroindeno[7,1,2-*pqr*]-*as*indaceno[3,2,1,8,7-*defghi*]chrysene ( $C_{28}H_{14}$ , Figure 1(a)), that is one of the hitherto unexplored bowl-shaped fragments of buckminsterfullerene ( $C_{60}$ , Figure 1(b)). There is no hit in SciFinder in searching its  $C_{28}H_{14}$  structure (July 1st, 2024). The nona-cycle fuses structurally together with a hexa-cyclic dibenzo[*g*,*p*]chrysene ( $C_{26}H_{16}$ , DBC, Figure 1(c)) and threefold five-membered rings at its *bay* and *cove* areas. Our synthetic outline to the nona-cycle skeleton is depicted in Scheme 1, where the key compounds are starting DBC 1 and *iso*-1,<sup>[15]</sup> and intermediates 2 and 3, and target molecule 4. The crucial steps



(3,10-dihydroindeno[7,1,2-pqr]-as-indaceno[3,2,1,8,7-defghi]chrysene)



**Figure 1.** (a) Nona-cycle  $C_{28}H_{14}$  of 3,10-dihydroindeno[7,1,2-*pqr*]-*as*-indaceno[3,2,1,8,7-*defghi*]chrysene, and (b)  $C_{60}$  of buckminsterfullerene, and (c) hexa-cycle  $C_{26}H_{16}$  of dibenzo[*g*,*p*]chrysene.

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Scheme 1. Synthetic outline from *bay*-brominated DBC 1/*iso*-1 and octa-cyclic polyarenes 2 and 3 to nona-cyclic 4 and/or deca-cycle molecules.

were located in formation of five-membered rings of 2 and 4. For 1/iso-1 to 2, we supposed that if the bromine atoms were transformed into carboxylic acid, intramolecular Friedel-Crafts acylation could introduce two pentagons into the *bay* regions of 2. For 3 to 4, it was envisaged that the opposing two bromines could undertake homo-coupling reaction protocol to complete nona- and/or deca-cycle buckybowls.

#### **Results and Discussion**

At the outset of our study, dibromide 1/iso-1 was derived from a 2,7-dimethoxy-9-fluorenone (Scheme 2).<sup>[16]</sup> Upon addition of AlCl<sub>3</sub> to the fluorenone in *iso*-propyl chloride solvent, the



Scheme 2. Synthesis of an isomeric mixture of DBC 1 and *iso*-1 through intermediate 5, 6, and 7/*iso*-7.

Friedel-Crafts alkylation occurred selectively at 3- and 6positions to give **5** in 48% yield. Mono-bromination of **5** proceeded, giving regio-defined **6** in 74% yield. Refluxing solvent of tri-*iso*-propyl phosphite ( $P(OiPr)_3$ ) united two molecules of **6** to yield a dimerized spiro-ketone of **7**/*iso*-**7** in 94% with molar ratio of 51:49.<sup>[17]</sup> The ketone undertook reduction by NaBH<sub>4</sub>, and the corresponding alcohol was subjected to acid-mediated migration reaction in 89% yield with 31 grams: thus, the multi-substituted DBC **1**/*iso*-**1** was compatible with multi-gram scale technique.

The route for the synthesis of octa-cycle diketone 2 is shown in Scheme 3. The approach is based on the ring-closing reaction engaged upon intramolecular Friedel-Crafts acylation at the bay. The bromine-lithium exchange reaction in solutionphase at low -78°C between 1/iso-1 and n-butyllithium, followed by the nucleophilic attack to gaseous carbon dioxide, provided the dicarboxylic acid. The acid sufficiently tolerated purification using silica-gel column chromatography, giving 76% yield of 8/iso-8 in pure form. Reaction of 8/iso-8 with thionyl chloride (SOCl<sub>2</sub>) afforded quantitative formation of the corresponding acid chloride. The acid chloride was so moisturesensitive that we consecutively performed the Friedel-Crafts acylation reaction, and the high-yielding cyclization made the advanced polyarene 2 in 74% with 10 grams. Although the prior products consisted of two isomers, the isomers converged on single molecule 2 that was readily soluble and could be elaborated on multi-gram scale.

The molecular structure of **2** was confirmed by X-ray crystallographic analysis, which made apparent a newly built bis-pentagons (Figure 2(a)).<sup>[18]</sup> The *sp*<sup>2</sup>-hybridized carbon atom of the carbonyl group binds the two aryl moieties with two bonds, which forcibly sets six-membered rings at interior angles of less 113.0° and 117.3° than regular angle 120° (Figure 2(b)). The smaller values inevitably widen the frontage of *cove* areas, so that the decreased repulsion of two protons at the *cove* twists the whole molecule **2** in less torsion angle of about 12.6° than 28.6°~37.3° that are conventional DBC angles in Nakamura's report:<sup>[19]</sup> actually, the  $\pi$ -conjugated surface in **2** looks almost flat architecture (Figure 2(c) and (d)).

The solution-processable path to tetra-brominated **3**, that is a key precursor, is shown in Scheme 4. The diketone **2** engaged in deoxygenation reaction by AlCl<sub>3</sub> and NaBH<sub>4</sub> to yield **9** in 71%,<sup>[20]</sup> wherein the *sp*<sup>3</sup>-hybridized carbon atom of methylene moiety bridged two aryls. Although we attempted to convert **9** into **3** directly, the regio-defined fourfold bromination reaction was not observed. The conventional demethylation of **9** by BBr<sub>3</sub>



Scheme 3. Synthesis of octa-cycle 2 through the dicarboxylic acid 8/iso-8.





**Figure 2.** Molecular structures with ORTEP drawing of **2** with thermal ellipsoids at the 50% probability level (the hydrogen atoms are omitted for clarity); (a) top view, wherein torsion angle determined by the four carbon atoms of intersectional naphthalene C<sup>01</sup>, C<sup>02</sup>, C<sup>03</sup>, and C<sup>04</sup> was 12.58(13)°; (b) description of selected angles and bond-lengths; (c) side view from a *cove* area (methyl ether substructures are removed for ease of viewing); (d) sideview from a ketone moiety (*iso*-propyl groups are omitted for ease of viewing).



Scheme 4. Synthesis of tetra-bromide 3 through 9, 10, and 11.

gave tetrol **10** in 85% yield, followed by sterically demanding fourfold bromination at the two *cove* regions to afford full-substituted DBC **11** in 73% yield. The final methylation reactions occurred quadruply in the presence of Meerwein's salt (Me<sub>3</sub>OBF<sub>4</sub>) and Proton Sponge (1,8-bis(dimethylamino)naphthalene), which produced 4.5 grams of **3** in 83% yield.

With the amounts of **3** in hand, the ring-closure at *cove* through activation of bromines to yield the corresponding nona- (**4**) and/or deca-cycle products was attempted. However, a lot of laborious work for the pentagon formation was unsuccessful: Yamamoto coupling method by Ni-mediated protocols, bromine-lithium exchange reaction by organolithium reagents, and radical approach by using AIBN (azobis(isobutyronitrile)) resulted in the messy products including **9** and didn't generate only deca-cyclic product but also

nona-cycle 4.[21] Alternatively, we decided to employ Pdmediated transformations, and tested a variety of palladium complexes and external ligands. As a result, Only Pd[P(t-Bu)<sub>3</sub>]<sub>2</sub> reagent cyclized the one-side cove region to form 4 (Scheme 5).<sup>[22]</sup> The bridge-building needed high reaction temperature of refluxing mesitylene, which elaborated yielding 4 in 24% along with 32% of unreacted 3. Why was the cyclization reaction so difficult? Why was the second ring-closing to form the deca-cycle adduct unachievable? Currently, the mechanistic reason remains unclear. However, in our previous report,<sup>[14]</sup> we successfully activated the four bromine atoms of a hexa-cycle tetrabromide lacking the two methylene moieties of 3, and reasonably induced twofold pentagons to synthesize the corresponding octa-cycle buckybowl. Thus, these suggest that the two methylenes in 3 diminished the flexibility and consequently made the cyclization less likely to occur.

X-ray crystallographic analysis elucidated the molecular structure of 4 having three pentagons and two bromine atoms (Figure 3(a)).<sup>[23]</sup> We measured bond-lengths and bond angles (Figure 3(b)): the intersectional 6:6-bond distance was ca. 1.39 Å that is also observed in C<sub>60</sub>, and the cove region around the bromines was distorted at interior angles of 111.9° and 116.5° (Figure 3(b)). In side view from a cove area (Figure 3(c)), the two bromines rebelled against each other, and the  $\pi$ conjugation around the cove was heavily twisted with torsion angle of 35.2° (Figure 3(d)). On the other hand, the newly built pentagon made the gently curved and definitely caved  $\pi$ surface sculpting at 1.718 Å interval that consists of 1.218 Å bowl-depth and 0.480 Å distance (Figure 3(e) and (f)). Haddon's  $\pi$ -orbital axis vector (POAV) analysis of the X-ray data revealed that the two carbons of the intersectional 6:6-bond are pyramidalized to  $3.6^{\circ}$  (outer carbon, close to bromines) and  $6.0^{\circ}$ (inner carbon).<sup>[24,25]</sup> Thus, nona-cycle **4** proved to be a distinctive configuration characterized by the coexistence of a bowl-shape and a twist-form. This contradictory arrangement might hinder the activation of two bromines in 4, resulting in non-formation of the deca-cycle.

Packing views of **4** were also obtained (Figure 4). Although the deep bowl-shaped  $\pi$ -aromatics are known to favor a stacking architecture in a concave-convex fashion, such an arrangement was not observed in **4** presumably due to the multiple substituents (Figure 4(a)).<sup>[5,26]</sup> The  $\pi$ -surfaces were not overlapping but are slightly shifted and stacked on top of each other. In Figure 4(b), methyl groups in the methoxy and *iso*propyl moieties seem to interact with another concave surface



**Scheme 5.** Synthesis of nona-cycle **4** through  $Pd[P(t-Bu)_3]_2$ -mediated intramolecular cyclization of **3**.





**Figure 3.** Molecular structures with ORTEP drawing of 4 with thermal ellipsoids at the 50% probability level (the hydrogen atoms are omitted for clarity); (a) top view; (b) description of selected angles and bond-lengths (methyl ethers and *iso*-propyl groups are removed for ease of viewing); (c) side view from a *cove* area of two bromine atoms (methoxy substructures are removed for ease of viewing); (d) torsion angle that is determined by the four carbon atoms of C<sup>1</sup>, C<sup>2</sup>, C<sup>3</sup>, and C<sup>4</sup>; (e) side view from a methylene moiety with description of the bowl-depth and distance from the intersectional 6:6-bond (substituents except bromines are omitted for clarity); (f) side view from a slanting upper part (all substituents at the periphery are omitted for ease of viewing).



**Figure 4.** Molecular packing structures with ORTEP drawing of **4** (the hydrogen atoms are omitted for clarity): (a) top view (*iso*-propyl groups and methoxy moieties are removed for ease of viewing), and (b) side view from methoxy groups with description of intermolecular distances.

with the stacking distance of approximately 3.3 Å. Based on these discussion, it can be understood that the definite presence of these concave and convex surfaces causes differences in the chemical shifts of methylene protons in **4**: two sets of AB-shaped doublet peaks of 4.83 ppm (d, J=20 Hz, 2H) and 4.54 ppm (d, J=20 Hz, 2H) were observed, although other methylene protons in **9**, **10**, **11**, and **3** appeared as singlet peaks. The up-field shifted protons were oriented towards the concave face and the down-field ones towards the convex, because the up-field shift was caused by anisotropic effect of concave aromatic pi-clouds.

Following this discussion, we calculated the mappings and energies for frontier orbitals of **4** and the unsubstituted nonacycle, using DFT method (B3LYP–D3/6-31G(d,p) (Figure 5).<sup>[27]</sup>



Figure 5. Orbitals mappings (LUMO, HOMO, and HOMO-1) and the energies for (a) 4 and (b) unsubstituted one.

The structural optimization of compound 4 was performed using X-ray crystallography as an initial structure. The optimized structure reproduced both the helicene and bowl structures. In contrast, the unsubstituted nona-cycle exhibited a bowl-shaped  $C_s$  symmetric structure, but not a helicene-like twisted structure. Regarding the molecular orbitals, the LUMO mappings of 4 and the unsubstituted one were almost identical. This indicates that the LUMO mapping trend is not affected by the helicenederived unsymmetrical substructure. The contribution of the benzo[*qhi*]fluoranthene moiety (penta-cycle substructure) is significant. For the HOMO and HOMO-1, 4 exhibited unsymmetrical distribution, with the orbitals located on one side each. On the other hand, in the unsubstituted one, both were symmetrically distributed. Thus, HOMO trend proved to be profoundly impacted by helicene-derived unsymmetrical structure. In terms of energy, 4 exhibited a higher HOMO and a lower LUMO compared to the unsubstituted one, resulting in a smaller HOMO-LUMO gap. This implies that 4 will be more reactive than the unsubstituted one.

Finally, to advance our understanding of structural chemistry, the POAV angles of nona-cycle 4 were compared with those of related fused-rings, for example, illustrated in Figure 6. The data are summarized in Table 1. Parent C<sub>60</sub> gives 11.6° (Entry 1),<sup>[28,31]</sup> and typical buckybowls of DIC,<sup>[5,14]</sup> sumanene,<sup>[29]</sup> and corannulene<sup>[28,30]</sup> at the bottom carbon exhibit 9.0°, 9.0°, and 8.2°, respectively (Entries 2-4). The POAV  $3.6^{\circ}$  and  $6.0^{\circ}$  for 4 were found to be smaller than those, particularly, DIC 9.0° (Entry 5). From the perspective of comparison with DIC, the two pentagons in a DIC cause deeper container shape than three pentagonal rings in 4. On the other hand, the skeleton of 4 can be seen to include fragments of corannulene and sumanene (Figure 6(b) and (c)). The former is penta-cycle and the latter hexa-cycle, which are already reported with crystallographic drawings.<sup>[32,33]</sup> Interestingly, those fragments are so flat (POAV,  $< 0.9^{\circ}$ ) (Entries 6–7, Figure 2S). Compared to these planar polyarenes, a curved geometry of



**Figure 6.** (a) Buckybowls of diindeno(1,2,3,4-*defg*:1',2',3',4'-*mnop*)chrysene (DIC), sumanene, and corannulene; (b) flat-shaped corannulene fragment,<sup>[32]</sup> that is corresponding to the black line part in **4**; (c) flat structure of sumanene fragment, that is corresponding to the black line frame in **4**.<sup>[33]</sup>

| Table 1. POAV angles of fused-rings illustrated in Figure 6.                    |                    |   |
|---|--------------------|---|
| Entry   | Fused-ring         | POAV/° <sup>[b]</sup>                     |
| 1   | C <sub>60</sub>    | 11.6                                      |
| 2   | DIC <sup>[a]</sup> | 9.0                                       |
| 3   | Sumanene           | 9.0                                       |
| 4   | Corannulene        | 8.2                                       |
| 5   | 4                  | 3.6 <sup>[c]</sup> and 6.0 <sup>[d]</sup> |
| 6   | Corannulene frag.  | ~0.9 <sup>[e]</sup>                       |
| 7   | Sumanene frag.     | ~0.6 <sup>[f]</sup>                       |
| [2] DIC: diindeno(1.2.3.4-defa:1'.2'.3'.4'-mnon)chrysene [b] $\pi$ orbital axis |                    |   |

[a] DIC; diindeno(1,2,3,4-*defg*:1',2',3',4'-*mnop*)chrysene. [b]  $\pi$  orbital axis vector. [c] Outer carbon. [d] Inner carbon. [e] CCDC-1874124. [f] CCDC-1290159.

nona-cycle **4** was caused by increase in the number of rings. Thus, those may be informative for creating contorted nonplanar polycycles.

## Conclusions

In conclusion, we have synthesized one of the hitherto unexplored buckybowls, wherein the solution-phase synthesis of fourfold methoxy- and alkyl-anchored nona-cyclic **4** was achieved. Such a type of multi-substituted and solution-processable nona-cyclic buckybowl has no counterparts in the organic synthetic realm. The key to success lies in the design of solution-compatible approach to ring-closure at the *bay* and *cove* areas of dibenzo[*g*,*p*]chrysene core. Our results suggest the following three salient features: One, solution-processable hexa-cycle **1**/*iso*-**1** was amenable to double pentagon formation at the *bay* areas in multi-gram scale by means of intra-molecular

Friedel-Crafts acylation. Two, the fully substituted octa-cycle 3 underwent ring-closure at the cove site, giving a nona-cyclic curvature 4. Three, its crystallographic study, coupled with the computational assistance, elucidated the structural features. Although the final step from 3 to 4 awaits improvement, this synthetic performance would provide a guiding principle in creating multi-substituted solution-manageable polycycles. Additionally, the structural comparison of nona-cycle 4 with corannulene and sumanene fragments afforded considerable insights into the skeletal requirements for making the bowl shape. This information is highly relevant to research aimed at creating new non-planar pi-conjugated molecules. Because non-planar polyarenes can be functional organic materials those would be applicable to ongoing research and future technology.<sup>[34-36]</sup> Further development of solution-compatible scheme for C<sub>60</sub>-fragments is ongoing and will be reported in due course.

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## **Experimental Section**

Synthesis of 6,7-dibromo-2,4,9,11-tetraisopropyl-1,5,8,12-tetramethoxy-3,10-dihydroindeno[7,1,2-pqr]-as-indaceno[3,2,1,8,7defghi]chrysene (4). Under an argon atmosphere, to a solution of 3 (1.00 g, 1.05 mmol) in mesitylene (20.0 mL) was added bis(tri-tertbutylphosphine)palladium(0) (534 mg, 1.05 mmol). The reaction mixture was allowed to warm to 195 °C (bath temp.), then stirred for 15 h. The mixture was allowed to cool to ambient temperature, and filtered through a pad of celite. The organic phase was washed with brine (50 mL), and dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo to give crude products as brown solid materials. Purification by short-plugged silica-gel column chromatography (Hexane/ Toluene, 1:2) afforded 191 mg of yellow solid materials (24%). Data: Rf value 0.53 (Hexane/Toluene, 1:19); M.p. 235 °C (dec.); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 4.83 (d, J=20 Hz, 2H, CH<sub>2</sub>), 4.54 (d, J=20 Hz, 2H, CH<sub>2</sub>), 4.32 (s, 6H, OCH<sub>3</sub>), 4.21 (s, 6H. OCH<sub>3</sub>), 3.84 (qq, J=7.0, 7.0 Hz, 2H, C<u>H</u>(CH<sub>3</sub>)<sub>2</sub>), 3.76 (qq, J=7.0, 7.0 Hz, 2H, C<u>H</u>(CH<sub>3</sub>)<sub>2</sub>), 1.62 (d, J = 7.0 Hz, 6H, CH(C<u>H\_3</u>)<sub>2</sub>), 1.60 (d, J = 7.0 Hz, 6H, CH(C<u>H\_3</u>)<sub>2</sub>), 1.50 (d, J = 7.0 Hz, 6H, CH(C<u>H\_3</u>)<sub>2</sub>), 1.47 (d, J = 7.0 Hz, 6H, CH(C<u>H\_3</u>)<sub>2</sub>) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 158.1 (C-5), 156.2 (C-1), 142.9 (C-3a), 142.3 (C-2a), 139.6 (C-4), 139.0 (C-2), 138.2 (C-6a), 137.3 (C-6b1), 134.4 (C-12b<sup>1</sup>), 130.9 (C-2a<sup>1</sup>), 129.6 (C-3a<sup>1</sup>), 125.3 (C-12b), 122.5 (C-6b), 118.2 (C-6), 64.7 (OCH<sub>3</sub>), 63.4 (OCH<sub>3</sub>), 41.7 (CH<sub>2</sub>), 29.2 (<u>C</u>H(CH<sub>3</sub>)<sub>2</sub>), 28.7 (<u>C</u>H(CH<sub>3</sub>)<sub>2</sub>), 23.6 (CH(<u>C</u>H<sub>3</sub>)<sub>2</sub>), 23.3 (CH(<u>C</u>H<sub>3</sub>)<sub>2</sub>), 22.90 (CH(<u>C</u>H<sub>3</sub>)<sub>2</sub>), 22.86 (CH(<u>CH</u><sub>3</sub>)<sub>2</sub>) ppm; MS (DART-TOF) *m/z*: 795 [MH]<sup>+</sup>; IR (neat): 2963, 2929, 2869, 2836, 1573, 1541, 1443, 1362, 1304, 1231, 1018, 640, 583 cm<sup>-1</sup>; HRMS (DART-TOF) calcd. for  $C_{44}H_{45}Br(79)_2O_4$  [MH]<sup>+</sup>: 795.1685, found: 795.1704.

Deposition Numbers 2160145 (for **2**) and 2242952 (for **4**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe, http://www. ccdc.cam.ac.uk/structures, Access Structures service.

# **Supporting Information Summary**

Further data are available in the supplementary material of this article.



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# **Conflict of Interests**

The authors declare no conflict of interest.

# Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

**Keywords:** Polycycles  $\cdot$  Buckybowls  $\cdot C_{60}$  fragments  $\cdot$  Non-planar  $\pi$ -conjugation  $\cdot$  Dibenzo[q,p]chrysenes

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(for 2). Monoclinic, space group P 1 21/c 1, colorless, a = 14.1922(3) Å, b=25.3492(5) Å, c=9.8426(2) Å,  $\alpha$ =90°,  $\beta$ =103.939(2)°,  $\gamma$ =90°, V=3436.71(12) Å3, Z=4, T=93 K, dcalcd.=1.293 gcm<sup>-3</sup>,  $\mu$ (Mo–K $\alpha$ )= 0.676 mm<sup>-1</sup>, R1=0.0455, wR2=0.1373, GOF=1.123.

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# **RESEARCH ARTICLE**



Relevant synthesis to an unexplored nona-cycle buckybowl (C<sub>28</sub>H<sub>14</sub>, 3,10dihydroindeno[7,1,2-pqr]-asindaceno[3,2,1,8,7-defghi]chrysene) is described. The key precursor is a solution-processable hexacycle having



twofold bromines and fourfold ethers. The bromines enabled forming the first two pentagons, and then the ethers facilitated yielding the nonacycle C<sub>60</sub>-fragmentary bowl-structure, unattainable so far.

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**Construction of Multiple Five-**Membered Rings in Dibenzo[g,p]chrysene Core for the Synthesis of a Nona-Cycle Buckybowl