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ARTICLE

A practical synthesis and X-ray crystal structure of tribenzo[*a*,*d*,*j*]corannulene

Natalie J. Smith and Lawrence T. Scott

Abstract: Tribenzo[*a*,*d*,*j*]corannulene (**5**) has been synthesized in four linear steps from commercially available starting materials on a half-gram scale in 18% overall yield. An X-ray crystal structure of this triply benzannulated geodesic polyarene confirms the prediction that successive benzannulation of corannulene has a gradual flattening effect on the bowl-shaped core.

Key words: benzannulation, geodesic polyarene, polycyclic aromatic hydrocarbon.

Résumé : Nous avons synthétisé le tribenzo[*a*,*d*,*j*]corannulène (**5**) en quatre étapes linéaires à partir de produits de départ commerciaux à l'échelle d'un demi-gramme dans un rendement global de 18 %. Une analyse par radiocristallographie de la structure de ce polyarène géodésique fusionné à trois anneaux de benzène confirme la prédiction que les benzannélations successives du corannulène ont un effet aplanissant graduel sur la partie centrale en forme de bol. [Traduit par la Rédaction]

Mots-clés : benzannélation, polyarène géodésique, hydrocarbure aromatique polycyclique.

Introduction

The pioneering research of Reginald Mitchell on benzannulations of aromatic π-systems[1] inspired us to extend those studies to corannulene (**1**), the benzannulated homologues of which constitute a unique family of curved polycyclic aromatic hydrocarbons (PAHs; **2–8**, Fig. 1).

Thanks to the work of Siegel and co-workers, the parent corannulene (**1**) is now available in kilogram amounts.[2] With the lone exception of our gram-scale synthesis of dibenzo[*a*,*g*]corannulene (**3**),[3] however, none of the benzannulated corannulenes has ever been prepared and isolated in more than milligram quantities, and no syntheses of tetrabenzocorannulene (**7**) or pentabenzocorannulene (**8**) have ever been published. Herein, we report the first practical synthesis of tribenzo[*a*,*d*,*j*]corannulene (**5**).[4]

The first milligram quantities of the title compound (**5**) were synthesized, isolated, purified, and characterized in 1997 by a talented undergraduate student in this laboratory, Brandon McMahon, as part of his senior thesis project (Fig. 2).[5] The use of flash vacuum pyrolysis (FVP) in the final step, however, limits the scale of this preparation to only tens of milligrams per run.

Several years later, Mehta and Srirama published a second synthesis of **5** that also employed FVP in the final step (Fig. 3).[6] Since then, no other syntheses of this $C_{32}H_{16}$ fullerene fragment have been reported.

Experimental

General

Commercially available chemicals were used as received without further purification unless noted. Dry solvents were purified using a Glass Contour solvent purification system. Silica gel chromatography was carried out using Sorbent Technology or Zeochem silica gel with a porosity of 60 Å and a particle size of 32–63 μm. NMR spectra were recorded in the Boston College Nuclear Magnetic Resonance Center on Varian instruments. NMR shifts are reported in ppm downfield from tetramethylsilane, using the solvent as the standard reference: chloroform-d_1 ($\delta_H = 7.26$ ppm, $\delta_C = 77.0$ ppm). High-resolution mass spectra were obtained in the Boston College Mass Spectrometry Center on a DART-TOF spectrometer operating in positive ionization mode. X-ray crystallography was performed at the Boston College X-ray Crystallography Center on a Siemens 3-circle geometry platform diffractometer with a Bruker APEX CCD area detector equipped with a copper source. Melting points are reported uncorrected.

Acephenanthrylene-4,5-dione (11)

In a flame-dried, 500-mL round bottom flask, 30.6 g (115 mmol) of aluminum bromide was dissolved in 200 mL of carbon disulfide. The solution was cooled to −40 °C, and a solution comprising 10.0 g (56.1 mmol) of phenanthrene and 5.30 mL (56.5 mmol) of oxalyl bromide in 80 mL of carbon disulfide was added slowly with stirring over 15 min. The reaction mixture was stirred at −40 °C for 3 h before being allowed to warm to room temperature. After being stirred for 1 h more, the mixture was poured carefully into water. It was then thoroughly extracted with dichloromethane. The organic solution was washed three times with water and once with brine, dried over magnesium sulfate, and concentrated to dryness. Column chromatography on silica gel eluted with dichloromethane gave 5.49 g (42%) of acephenanthrylene-4,5-dione (**11**) as a bright yellow solid. mp 242–245 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.86 (d, *J* = 8.1 Hz, 1H), 8.69 (d, *J* = 8.2 Hz, 1H), 8.35 (s, 1H), 8.17–8.13 (m, 2H), 7.95 (dd, *J* = 8.2 Hz, 7.2 Hz, 1H), 7.90 (ddd, *J* = 8.3 Hz, 7.0 Hz, 1.3 Hz, 1H), 7.79 (ddd, *J* = 8.1 Hz, 7.0 Hz, 1.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 188.6, 188.2, 142.9, 132.5, 131.8, 131.6, 130.3, 129.3, 129.0, 128.8, 128.7, 128.5, 125.9, 124.8, 123.1, 122.3. HRMS (DART-TOF) calcd for $C_{16}H_9O_2$ $(M+H)^+$: 233.0602; found: 233.0603 (lit.[7]).

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N.J. Smith and L.T. Scott. Merkert Chemistry Center, Department of Chemistry, Boston College, Chestnut Hill, MA 02467-3860, USA.

Corresponding author: Lawrence T. Scott (email: Lawrence.scott@bc.edu).

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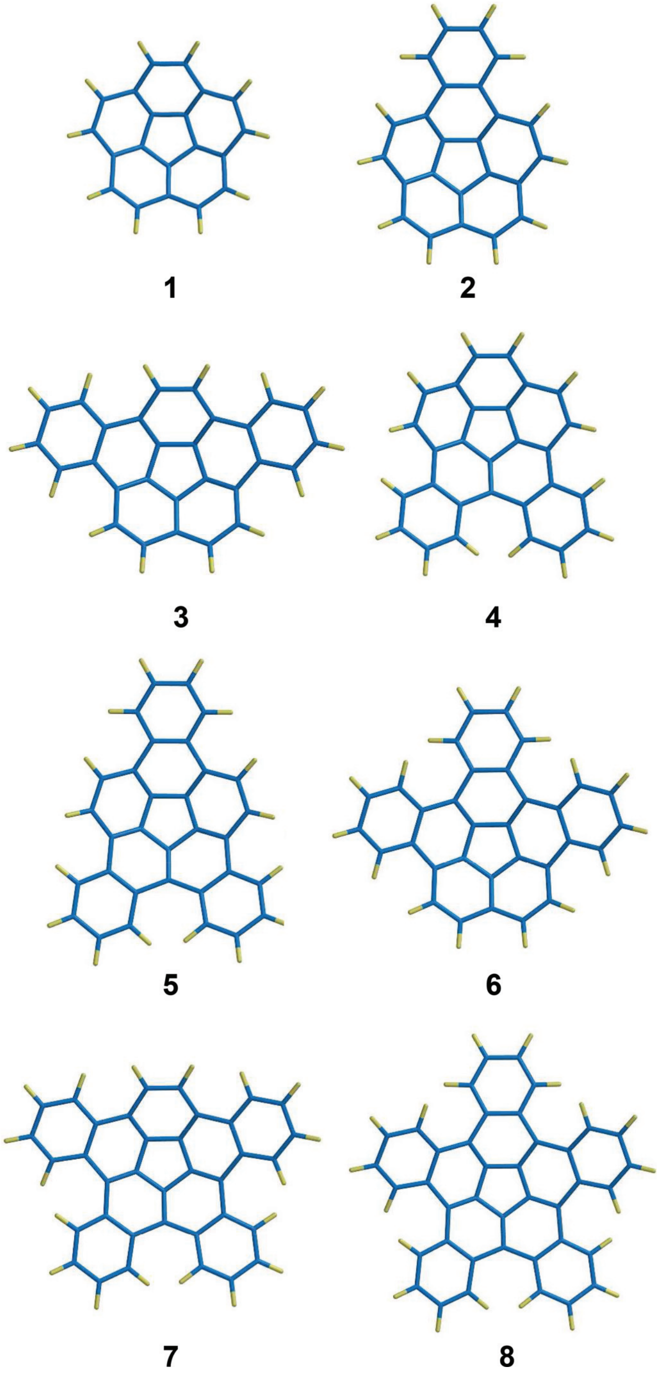
Fig. 1. Corannulene (**1**) and all of the possible benzannulated homologues. [Colour online.]



1,3-Bis(2-chlorophenyl)propan-2-one (13)

In a 500-mL, flame-dried, three-neck round bottom flask, 25 g (68.7 mmol) of diironnonacarbonyl was mixed with 200 mL of anhydrous benzene. After the addition of 8.7 mL (69 mmol) of 2-chlorobenzylchloride, the reaction mixture was heated to reflux for 24 h. The solution was allowed to cool to room temperature, filtered through a plug of silica gel, and flushed with dichloromethane. The solvent was removed under reduced pressure, and the crude material was recrystallized from hexanes to yield 5.21 g (18.6 mmol, 54%) of clean product (**13**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41–7.36 (m, 2H), 7.25–7.20 (m, 6H), 3.93 (s, 4H) (lit.[3, 8]).

Fig. 2. The first synthesis of tribenzo[*a*,*d*,*j*]corannulene (**5**).[5]

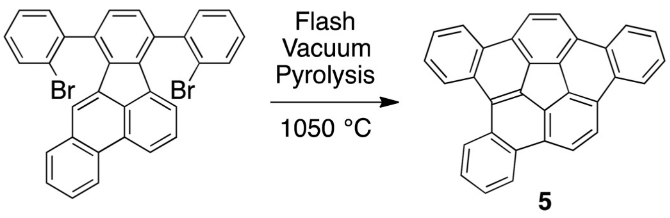
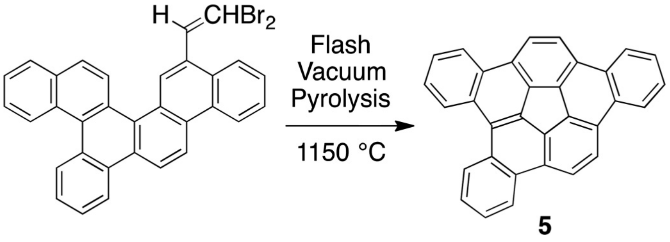


Fig. 3. The second synthesis of tribenzo[*a*,*d*,*j*]corannulene (**5**).[6]



9,11-Bis(2-chlorophenyl)-10*H*-cyclopenta[*e*]acephenanthrylen-10-one (14)

In a 125-mL Erlenmeyer flask, 1.20 g (4.31 mmol) of 1,3-bis(2-chlorophenyl)propan-2-one (**13**) and 1.00 g (4.31 mmol) of acephenanthrylene-4,5-dione (**11**) were mixed in a solution of 0.405 g (7.22 mmol) of potassium hydroxide in 36 mL of methanol. The reaction mixture was stirred at room temperature for 4 h, during which time a dark precipitate formed. The mixture was left standing overnight without stirring to allow the product to precipitate fully before it was collected by vacuum filtration and dried to yield 1.69 g (3.56 mmol, 82%) of pure product (**14**) as a dark purple solid. mp 205–212 °C (mixture of two atropisomers melts in two stages). ^{1}H NMR (500 MHz, $CDCl_3$, for a mixture of diastereomers) δ (ppm): 8.62 (d, *J* = 8.0 Hz, 1H), 8.57 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 7.9 Hz, 1H), 7.82 (d, *J* = 5.0 Hz, 1H), 7.76–7.54 (m, 8H), 7.47–7.37 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$, for a mixture of two atropisomers δ 199.8, 199.5, 156.8, 156.6, 155.3, 155.2, 142.8, 134.2, 134.1, 133.1, 132.1, 132.0, 131.7, 131.6, 131.0, 130.4, 130.11, 130.05, 129.97, 129.6, 129.5, 128.9 (broad), 128.8, 128.5, 127.9, 127.3, 126.6 (broad), 125.0, 124.8, 124.4, 124.2, 124.1, 122.8, 120.0 (broad), 119.0. HRMS (DART-TOF) calcd for $C_{31}H_{17}Cl_2O$ $(M+H)^+$: 475.0656; found: 475.0640.

7,10-Bis(2-chlorophenyl)benzo[*b*]fluoranthene (9)

(a) From the reaction of 14 *with 2,5-norbornadiene*

In a 5-mL round bottom flask, 318 mg (0.669 mmol) of 9,11-bis(2-chlorophenyl)-10*H*-cyclopenta[*e*]acephenanthrylen-10-one (**14**) was stirred in 1.0 mL of 2,5-norbornadiene at reflux for 5 days. After allowing the reaction mixture to cool to room temperature, the excess 2,5-norbornadiene was removed under reduced pressure. The product was purified by filtration through a plug of silica gel with dichloromethane. The final purified product (**9**) was collected in greater than 98% yield (316 mg, 0.668 mmol).

(b) From the reaction of 14 *with nitroethylene*

In a flame-dried 250-mL round bottom flask with a reflux condenser, 3.97 g (8.35 mmol) of 9,11-bis(2-chlorophenyl)-10*H*-cyclopenta[*e*]acephenanthrylen-10-one (**14**) and 31.0 g (209 mmol) of phthalic anhydride were mixed in 100 mL of toluene. After the addition of 14.7 mL (209 mmol) of 2-nitroethanol, the reaction mixture was heated to 140 °C and stirred for 26 h. After allowing the reaction mixture to cool to room temperature, it was diluted with dichloromethane. The organic layer was washed three times with 10% aq. sodium hydroxide and three times with water before drying over magnesium sulfate and evaporation of the solvent. The crude residue was purified by flash chromatography on silica gel with 3:1 hexanes–dichloromethane. The product collected (**9**) weighed 2.78 g (5.87 mmol, 70%). Further elution with dichloromethane resulted in the recovery of 11% of the starting material. On a small scale, in a sealed tube at 140 °C, the yield by this method was 92%. CAUTION: a full equivalent of carbon monoxide gas is released in this reaction, which causes pressure buildup. The sealed tube method is not advised for large-scale runs of this reaction. mp 130–186 °C (mixture of two atropisomers melts in two stages). ^{1}H NMR (500 MHz, CDCl$_3$, for a mixture of 2 atropisomers) δ: 8.59 (d, *J* = 8.1 Hz, 1H), 8.41 (d, *J* = 8.2 Hz, 1H), 7.74–7.46 (m, 12H), 7.39–7.35 (m, 2H), 7.18 (s, 1H), 6.98 (d, *J* = 7.3 Hz, 1H). ^{13}C NMR (125 MHz, CDCl$_3$, for a mixture of two atropisomers) δ: 139.4, 139.32, 139.29, 138.4, 136.3, 136.21, 136.20, 135.40, 135.38, 134.78, 134.76, 134.24, 134.23, 133.76, 133.75, 133.63, 133.62, 132.3, 131.4, 131.2, 130.5, 129.90, 129.85, 129.82, 129.77, 129.42, 129.40, 129.35, 129.34, 129.27, 129.26, 128.64, 128.63, 128.0, 127.25, 127.24, 127.14, 127.12, 127.10, 127.07, 127.03, 126.5, 124.3, 122.8, 121.8, 121.7. HRMS (DART-TOF) calcd for $C_{32}H_{19}Cl_2$ (M+H)$^+$: 473.0864; found: 473.0846.

Tribenzo[*a*,*d*,*j*]corannulene (5)

In a flame-dried 150-mL pressure vessel containing a magnetic stir bar, 1.00 g (2.11 mmol) of 7,10-bis(2-chlorophenyl)benzo[*b*]fluoranthene (**9**) and 0.331 g (0.448 mmol) of Pd(PCy$_3$)$_2$Cl$_2$ were mixed in 9.0 mL of *N*,*N*-dimethylacetamide. After the addition of 9.5 mL (63 mmol) of 1,8-diazabicyclo[5.4.0]undec-7-ene, the pressure vessel was capped and placed in a 150 °C oil bath to stir for 3 days. The reaction mixture was allowed to cool to room temperature before filtering through a plug of neutral alumina and flushing with dichloromethane. As the solution was diluted with dichloromethane from flushing the plug, some of the product precipitated out. This solid was collected by vacuum filtration. The filtrate was washed twice with 10% aq. hydrochloric acid, once with water, and once with brine. The solvent was removed under reduced pressure, and the crude material was purified by recrystallization from chloroform. The total amount of clean product (**5**) collected weighed 476 mg (1.19 mmol, 56%). mp 302–304 °C. ^{1}H NMR (500 MHz, CDCl$_3$) δ: 9.36 (dd, *J* = 8.2 Hz, 1.3 Hz, 2H), 8.81 (dd, *J* = 7.8 Hz, 1.7 Hz, 2H), 8.68 (AA′ of AA′XX′, 2H), 8.38 (d, *J* = 8.6 Hz, 2H), 8.36 (d, *J* = 8.6 Hz, 2H), 7.85–7.78 (m, 4H), 7.76 (XX′ of AA′XX′, 2H). ^{13}C NMR (125 MHz, $C_2D_2Cl_4$) δ: 134.7, 134.5, 133.8, 133.6, 132.8, 132.7, 128.2, 127.9, 127.6, 127.3, 127.2, 126.6, 125.5, 125.1, 124.6, 124.3, 123.9. HRMS (DART-TOF) calcd for $C_{32}H_{17}$ (M+H)$^+$: 401.1330; found: 401.1325. X-ray quality crystals were grown by slow evaporation of carbon disulfide. See the supplementary material for X-ray crystal data.

Results and discussion

Capitalizing on the palladium-catalyzed, solution-phase intramolecular arylation strategy introduced by our laboratory for imposing curvature on planar PAHs,[3] we have successfully synthesized the title compound (**5**) on a half-gram scale, and the procedure is readily amenable to further scale-up (Fig. 4).[9] In the final step of this synthesis, intermediate **9** is stirred at 150 °C for 3 days in *N*,*N*-dimethylacetamide containing catalytic amounts of Pd(PCy$_3$)$_2$Cl$_2$ and several equivalents of 1,8-diazabicyclo[5.4.0]undec-7-ene. Tribenzo[*a*,*d*,*j*]corannulene (**5**) was obtained from this reaction in 56% isolated yield after recrystallization from chloroform (mp 302–304 °C). Starting from commercially available starting materials, hydrocarbon **5** is obtained by this route in four linear steps in 18% overall yield.

Figure 5 shows the steps used to prepare synthetic intermediate **9**. The synthesis of acephenanthrylene-4,5-dione (**11**) in one step from phenanthrene (**10**) has previously been reported only in the patent literature.[7] In our hands, however, the described procedure failed to deliver **11** in the reported yield. Thus, we devoted considerable effort to optimizing the direct conversion of **10** to **11**. In the end, double Friedel–Crafts acylation of **10** with oxalyl bromide, using AlBr$_3$ as the catalyst, at −40 °C in carbon disulfide resulted in a 42% isolated yield of **11**. Unfortunately, additional experimentation never improved this modest yield. On the positive side, the reaction is reproducible; it uses inexpensive starting materials and reagents, and it can easily be carried out on a multi-gram scale.

Fig. 4. The first practical synthesis of tribenzo[*a*,*d*,*j*]corannulene (**5**), requiring no flash vacuum pyrolysis.[9]

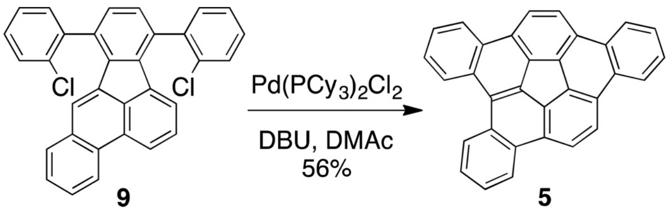
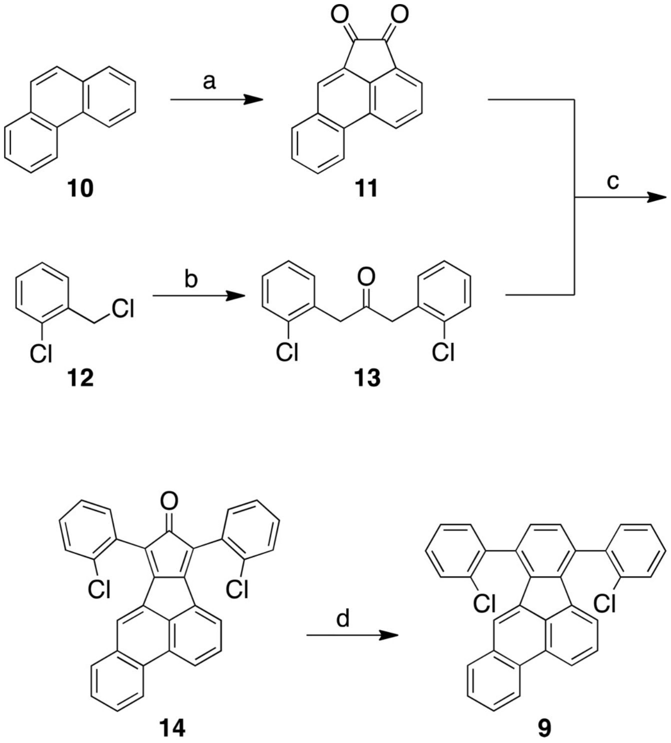


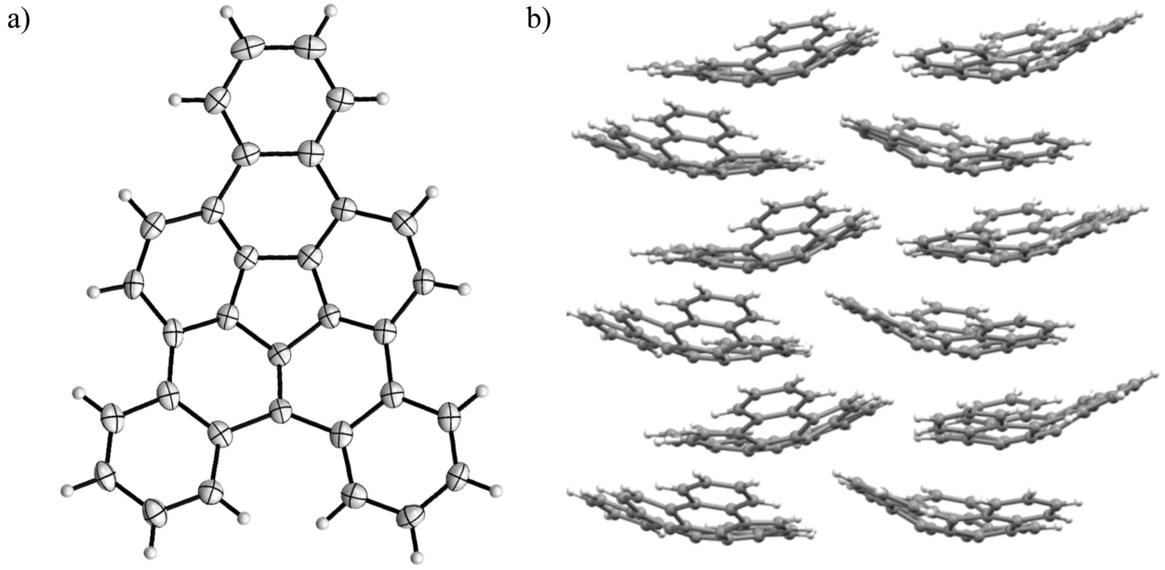
Fig. 5. Synthesis of intermediate **9** from commercially available starting materials: (*a*) oxalyl bromide, AlBr$_3$, CS$_2$, −40 °C, 42%; (*b*) Fe$_2$(CO)$_9$, benzene, 54%; (*c*) KOH, MeOH, 82%; (*d*) 2,5-norbornadiene, reflux, 99%, or 2-nitroethanol, phthalic anhydride, 140 °C, toluene, sealed tube, 92%.



The 1,3-bis(2-chlorophenyl)-2-propanone **13** was prepared by treating 2-chlorobenzyl chloride (**12**) with diironnonacarbonyl in hot benzene.[10] A double aldol condensation between **11** and **13**, catalyzed by potassium hydroxide in methanol, then gave the fused cyclopentadienone **14**, which could be isolated as a dark purple solid in good yield simply by filtration of the reaction mixture.[11]

Transformation of the cyclopentadienone ring in **14** into a benzene ring was achieved by Diels–Alder cycloaddition of a "masked acetylene," followed by chelotropic loss of carbon monoxide.[12] Two different masked acetylenes were examined. Nitroethylene, generated in situ from 2-nitroethanol by the action of phthalic anhydride in toluene at 140 °C in a pressure vessel,[13] adds rapidly to **14**, and the subsequent loss of carbon monoxide and HNO$_2$ gives **9** in 92% yield. Alternatively, refluxing **14** in neat 2,5-norbornadiene promotes an inverse electron demand Diels–Alder reaction, which

Fig. 6. X-ray crystal structure of tribenzo[*a*,*d*,*j*]corannulene (**5**), ORTEP ellipsoids at 50%. (*a*) Single molecule, top view. (*b*) Side view, showing stacking.



then delivers **9** almost quantitatively by loss of carbon monoxide and cyclopentadiene by a retro-Diels–Alder reaction.[12]

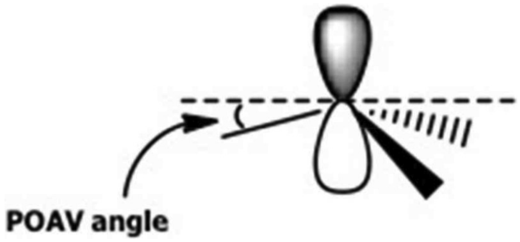
X-ray quality crystals of tribenzo[*a*,*d*,*j*]corannulene (**5**) were grown by slow evaporation of a carbon disulfide solution (Fig. 6). An examination of the experimental structural parameters confirms the prediction based on theoretical calculations that successive benzannulation of corannulene has a gradual flattening effect on the bowl-shaped core.[14]

Two metrics have come into common use for describing the curvature of bowl-shaped PAHs. One is the atom-by-atom π-orbital axis vector (POAV) analysis, popularized by Haddon,[15] and the other is the overall bowl depth.[16] The angle that each of the three bonds radiating from a trigonal carbon atom makes with the POAV of that carbon provides a well-defined measure of the pyramidalization of a quasi-sp^2 center. The angle is reported as the deviation of the carbon framework from a 90° angle with the π-orbital of the conjugated system, 90° being characteristic of planar sp^2 centers (Fig. 7). For the mono-, di-, and tri-benzannulated corannulenes, POAV angles are calculated for each of the unique carbon centres in the hub pentagon of the corannulene core. Table 1 lists the calculated (B3LYP/6–31G*) and experimental (X-ray) POAV angles for each of the hub carbon atoms of corannulenes **1**, **2**, **3**, and **5**, together with the averages of these POAV angles in each compound, for comparison purposes.

The second structural feature of interest is the bowl depth of each molecule. This value is defined as the shortest distance between the average plane of the five hub carbon atoms and the average plane created by the 10 carbon atoms on the corannulene rim. This measurement is a good indicator of the curvature of corannulene (**1**), benzo[*a*]corannulene (**2**), and dibenzo[*a*,*g*]corannulene (**3**); however, it is somewhat more ambiguous for the other members of the benzocorannulene family, owing to a significant "ruffling" of the corannulene core caused by adjacent benzo units. In those compounds, the 10 rim carbons no longer form an even plane, and the measure of curvature observed by this method may be distorted. Still, useful information can be gained about general trends in bowl depth, and the ruffling effect itself can offer interesting structural insights.

Table 1 demonstrates the good agreement between the calculated and experimentally determined POAV angles for **1**, **2**, and **5**. In contrast, the calculated values for dibenzo[*a*,*g*]corannulene (**3**) are significantly lower than those observed in the crystal structure, and the experimental bowl depth for **3** is almost identical to that for benzocorannulene (**2**). Nevertheless, a general trend can still be discerned. Both the POAV angles and the bowl depths decrease with an increasing number of benzo fusions. The addition of benzo groups to the rim of corannulene does indeed flatten the bowl, and calculations predict a continuation of this trend, with a particularly dramatic effect in the case of pentabenzocorannulene (**8**).

Fig. 7. π-Orbital axis vector angle.



Conclusion

The successful synthesis of tribenzo[*a*,*d*,*j*]corannulene (**5**) on a half-gram scale, in four linear steps and 18% overall yield, represents a significant step forward in the study of benzannulated curved PAHs. The key features of the synthesis are the efficient construction of a chlorinated precursor (**9**) and the introduction of curvature in the corannulene core through a pair of palladium-catalyzed, solution-phase cyclization reactions. An X-ray crystal structure of the title compound confirms the predicted trend that sequential benzannulation of corannulene leads to progressive flattening of the bowl.

Supplementary material

Supplementary material (NMR spectra of compounds **5**, **9**, **11**, **13**, and **14** and X-ray crystal structure CIF files for compounds **2** and **5**) is available with the article through the journal Web site at http://nrcresearchpress.com/doi/suppl/10.1139/cjc-2016-0516. CCDC 856219 contains the supplementary crystallographic data for this paper. These data can be obtained, free of charge, via http://www.ccdc.

Table 1. π-Orbital axis vector (POAV) angles and bowl depths of selected benzocorannulenes.

Structure	Compound	Calcd. POAV angles at hub (°)[a]	Avg. calcd. POAV angle (°)[a]	Exp. POAV angles at hub (°)	Avg. exp. POAV angle (°)	Bowl depth exp. (calcd.) (Å)
1	Corannulene[b]	8.1	8.1	8.6, 8.3, 8.3, 8.4, 8.3	8.4	0.87 (0.87)
2	Benzo[*a*]corannulene[c]	7.7, 7.8, 7.7	7.8	7.5, 8.0, 8.0, 8.2, 7.9	7.9	0.83 (0.82)
3	Dibenzo[*a*,*g*]-corannulene[d]	7.3, 7.3, 7.4	7.3	7.6, 7.7, 7.9, 7.8, 8.0	7.8	0.83 (0.77)
5	Tribenzo[*a*,*d*,*j*]-corannulene[e]	6.8, 6.3, 6.3, 6.7, 6.6	6.5	6.5, 6.3, 6.0, 6.6, 6.5	6.4	0.67 (0.68)
7	Tetrabenzo(*a*,*d*,*g*,*j*]-corannulene	5.8, 5.2, 5.2, 5.5, 5.2	5.4			(0.50)
8	Pentabenzo[*a*,*d*,*g*,*j*,*m*]-corannulene	3.8, 3.9, 3.9, 3.3, 4.2	3.8			(0.29)

[a] Calculated POAV angles at hub positions were obtained at the B3LYP/6–31 G* level of theory.
[b] X-ray: see ref. 17.
[c] X-ray: see ref. 18.
[d] X-ray: see ref. 19.
[e] X-ray: this work.

cam.ac.uk/products/csd/request/ (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. (Fax: 44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk)).

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