

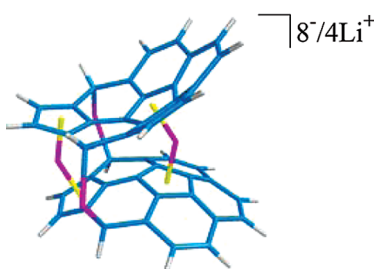
## Reduction of Bowl-Shaped Hydrocarbons: Dianions and Tetraanions of Annelated Corannulenes

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Received September 16, 2005



The reduction of several annelated corannulene derivatives was undertaken using lithium and potassium metals. It was found that annelation affects the annulenic character of corannulene by changing its charge distribution; the dianions of derivatives that are annelated with six-membered rings have less annulenic character and are less paratropic than corannulene dianion. This effect is even more pronounced in corannulenes that are *peri*-annelated with five-membered rings. The alkali metal used in the reduction process has a great influence on the outcome, especially on the degree of reduction. Most derivatives get reduced to tetraanions only with potassium, and not with lithium, the exception being systems that can stabilize the tetraanion with lithium by special means, such as aggregation or dimerization. One such system is cyclopenta[*bc*]corannulene (acecorannulylene), which gives a coordinative dimer that consists of two cyclopentacorannulene tetraanions, bound together in a convex–convex fashion by lithium cations. The points of contact in this dimer are two rehybridized carbons from each cyclopentacorannulene unit, which are bridged together by two lithium cations.

### Introduction

Polycyclic aromatic hydrocarbons (PAHs) represent a unique class of organic molecules because they combine the fascination of fullerene building blocks with the outstanding material properties of graphite and conducting polymers.<sup>1</sup> The planarity of these systems is often presumed to be their most significant geometric characteristic; however, molecules that deviate from this structural norm have also been synthesized and studied.<sup>2</sup> The discovery of fullerenes has rekindled interest in such curved molecules, especially those that can be mapped onto fullerene

surfaces;<sup>3</sup> however, the remarkable inner strain of these bent  $\pi$ -systems makes their synthesis arduous. In most cases, extreme

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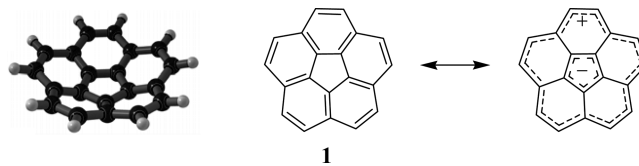
conditions such as flash vacuum pyrolysis (FVP) are required, although a few solution-phase syntheses have been reported.<sup>3</sup>

A much-studied aspect of such curved systems is their aromatic behavior,<sup>4</sup> for such systems can help clarify the nature of aromaticity as they manifest a compromise between strain and conjugation.<sup>3d,5</sup> One method for altering the aromatic character of PAHs is by reducing them with alkali metals.<sup>6</sup> Such reductions yield negatively charged  $\pi$ -conjugated molecules, which are interesting both synthetically and theoretically.<sup>6</sup> These anions not only have different aromatic character but they can also undergo structural changes that range from geometric distortions<sup>7</sup> and aggregation<sup>8</sup> to the formation of new chemical bonds.<sup>9</sup>

Addition of negative charge to such  $\pi$ -systems induces magnetic shielding on the nuclei, so NMR spectroscopy can be used to analyze the charge distribution. The charge density on the carbon  $\pi$ -framework is calculated using the differences in the <sup>13</sup>C NMR spectra of the anion and neutral species, employing eq 1<sup>10</sup>

$$\rho_{\pi} = \Delta\delta_{\text{C}}/K_{\text{C}} \quad (1)$$

where  $\rho_{\pi}$  is the change in the  $\pi$ -charge on the carbon and  $\Delta\delta_{\text{C}}$  is the chemical shift change for that carbon from the anionic to the neutral state.  $K_{\text{C}}$  is a calculated proportionality constant (calculated as the sum of differences in the chemical shifts, divided by the total charge of the anion) with a normal value



**FIGURE 1.** Corannulene ( $\text{C}_{20}\text{H}_{10}$ ), a bowl-shaped fullerene fragment and its annulene-within-an-annulene resonance structure.

of ca. 160.0 ppm/electron. However, ring current effects can induce large deviations from this value.<sup>11</sup>

Corannulene (**1**), the smallest curved subunit of  $\text{C}_{60}$ , was first synthesized by Barth and Lawton in 1966, using a tedious 17-step synthetic procedure.<sup>12</sup> Alternative and more efficient ways for synthesizing **1** were later developed by the groups of Scott,<sup>13</sup> Siegel,<sup>14</sup> and Zimmermann,<sup>15</sup> and these opened the way to the full investigation of **1** and its properties.<sup>16</sup> Barth and Lawton explained the aromaticity of **1** using the “annulene-within-an-annulene” model.<sup>12,17</sup> According to this model, **1** is made up of an aromatic cyclopentadienyl anion ( $6e^-/5\text{C}$ ) surrounded by an aromatic ( $14e^-/15\text{C}$ ) annulenyl cation (Figure 1).

The four-step reduction process of **1** with lithium metal has been thoroughly investigated by both NMR and ESR.<sup>8a,18</sup> As expected, the aromatic character of **1** changes as a function of the number of electrons added; the dianion ( $\mathbf{1}^{2-}$ ) is anti-aromatic ( $16e^-$  in the periphery), whereas the tetraanion ( $\mathbf{1}^{4-}$ ) is aromatic ( $18e^-$  in the periphery) as predicted by the “annulene-within-an-annulene” model.

It was found that the tetraanion  $\mathbf{1}^{4-}$  undergoes a fascinating self-assembly process and yields a highly charged supramolecular dimer ( $\mathbf{1}^{4-}/\mathbf{1}^{4-}/8\text{Li}^+$ ), which is “glued” together by

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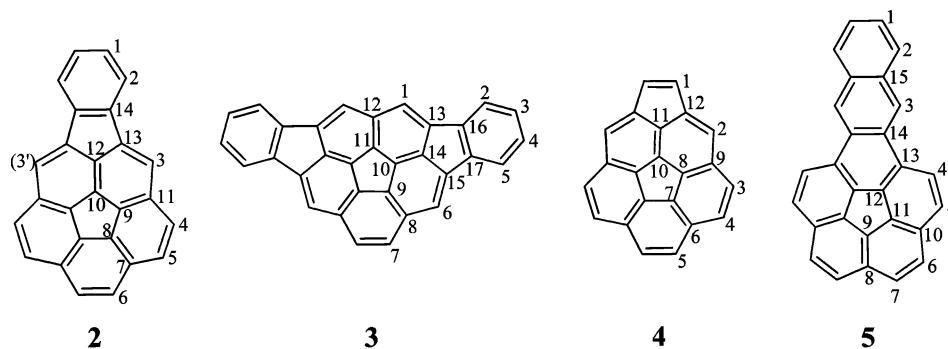
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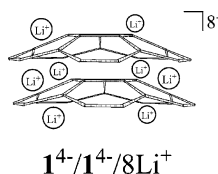
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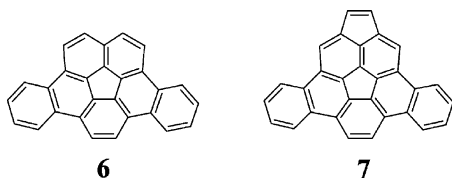


**FIGURE 2.** Compounds whose anionic states are studied by NMR spectroscopy in this work.

lithium cations.<sup>8a</sup> However, no dimerization takes place when **1** is reduced to a tetraanion with other alkali metals (potassium, rubidium, and cesium – sodium yields only a trianion radical).<sup>18f</sup> The dimer is formed only with lithium cations, presumably due to strong interactions between their large positive charge density and the high negative charge density in **1**<sup>4-</sup> (one electron per five carbon atoms).



Here, we wish to report the reduction with lithium and/or potassium metals of a series of corannulene derivatives that are annelated with five- or six-membered rings (5MRs and 6MRs, respectively), namely indenocorannulene (**2**),<sup>19</sup> diindeno[1,2,3-*bc*:1,2,3-*hi*]corannulene (**3**),<sup>20</sup> cyclopenta[*bc*]corannulene (**4**),<sup>21</sup> and naphtho[2,3-*a*]corannulene (**5**)<sup>22</sup> (Figure 2). Our motivation in this study was to investigate (a) the effect of annelation on the reduction and dimerization processes, (b) the effect of the alkali metal, (c) the differences in the aromatic/anti-aromatic characters of the derivatives, (d) the annulenic behavior of the derivatives of **1** as reflected in the  $K_C$  values, and (e) additional processes that these corannulene derivatives might undergo. A comparison was also made between the reduction of these derivatives with those of **1** and two other previously reduced derivatives, dibenzo[*a,g*]corannulene (**6**)<sup>23,24</sup> and dibenzo[*a,g*]cyclopenta[*kl*]corannulene (**7**).<sup>24,25</sup>



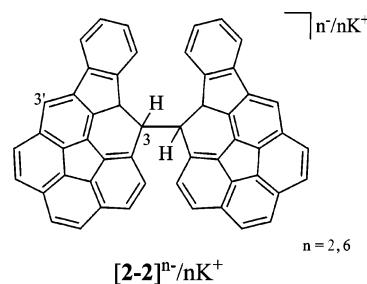
## Results and Discussion

**Syntheses of Diindeno[1,2,3-*bc*:1,2,3-*hi*]corannulene (3) and Naphtho[2,3-*a*]corannulene (5).** The new method for indenoannelation of polycyclic aromatic hydrocarbons that we reported in 2000<sup>26</sup> was used to synthesize the previously unknown diindeno[1,2,3-*bc*:1,2,3-*hi*]corannulene (**3**) for the first time.<sup>20</sup> Thus, two latent indeno groups were attached to corannulene (**1**) by Friedel–Crafts acylation with 2-bromobenzoyl chloride. As expected from our previous acylation of

corannulene with acetyl chloride,<sup>21b</sup> this reaction produced exclusively the 1,5- and 1,8-diacylcorannulenes (**8** and **9**, respectively) in a ratio of ca. 3:2. Without separation, the isomeric mixture of these two bis-(2-bromobenzoyl)corannulenes was subjected to flash vacuum pyrolysis. The resulting radical cyclization-decarbonylation cascade gave diindeno[1,2,3-*bc*:1,2,3-*hi*]corannulene (**3**) and diindeno[1,2,3-*bc*:1,2,3-*ef*]corannulene (**10**) in an 8:1 ratio, together with a substantial quantity of indenocorannulene (**2**), plus traces of corannulene (**1**) and other minor byproducts (Scheme 1).

Naphtho[2,3-*a*]corannulene (**5**) was synthesized by the classical annelation method illustrated in Scheme 2.<sup>20</sup> The other annelated corannulenes examined in this work have previously been reported.

**Indenocorannulene (2).** The reduction process of **2** with potassium has been briefly reported (Scheme 3).<sup>9b</sup> It was found that **2** undergoes an unprecedented four-step alternating reductive dimerization/bond-cleavage process. Covalent dimers are formed in the radical anion and trianion states via electron coupling between two carbon C3 atoms affording dianionic and hexaanionic covalent dimers, respectively (**[2-2]**<sup>n-/nK<sup>+</sup></sup>). The



formation of the new  $\sigma$ -bond was evident from the high field

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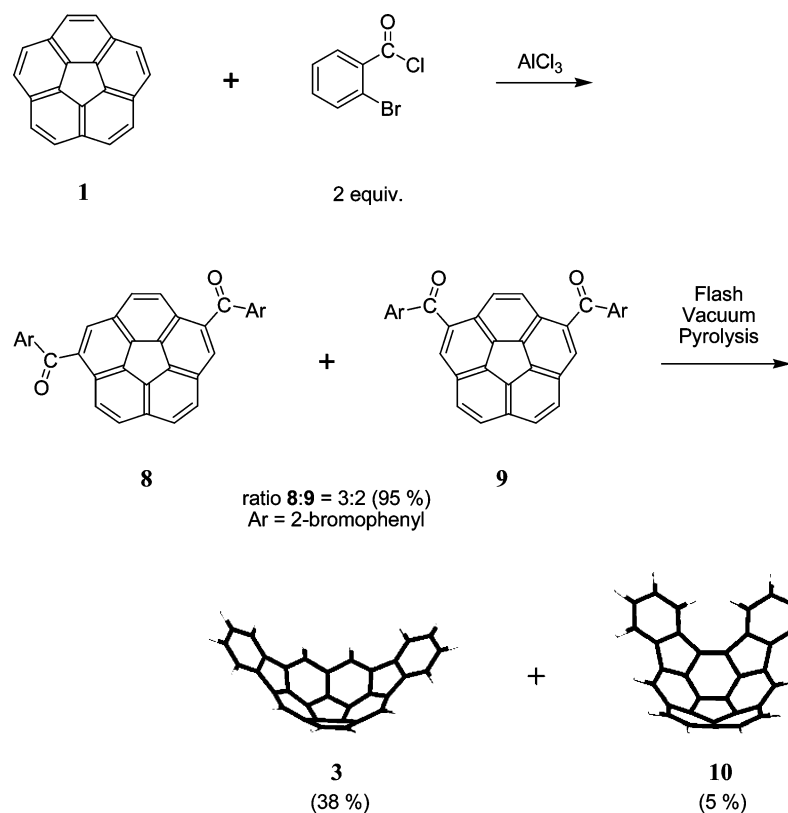
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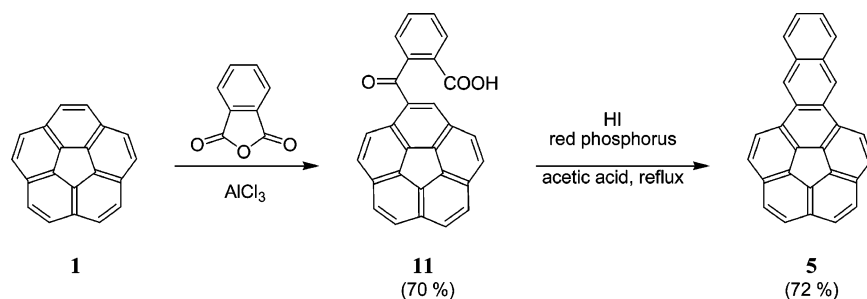
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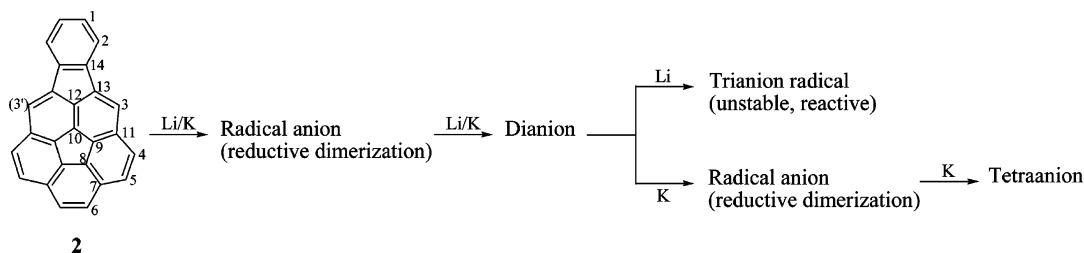
SCHEME 1



SCHEME 2



SCHEME 3



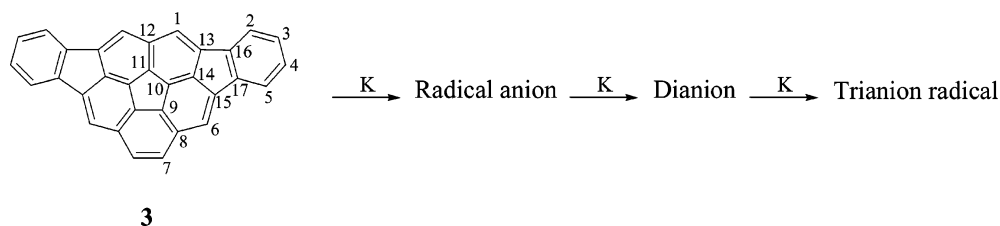
shift of carbon atom C3 (and proton H3) and its coupling constants ( $^1J_{\text{C,H}}$  and  $^3J_{\text{H,*H}}$ ). The electron coupling occurs at carbon atom C3 because a high spin density resides there in both the radical anion and the trianion radical, according to DFT calculations.<sup>9b</sup>

The story is somewhat different with lithium, where only three reduction steps are observed (Scheme 3). The first reduced species is a radical anion that undergoes a reductive dimerization process similar to that observed with potassium ( $[\text{2}^{2-}]^{2-}/2\text{Li}^+$ ). However, the product is hardly soluble, and therefore, only the  $^1\text{H}$  NMR of the covalent dimer could be measured. The low

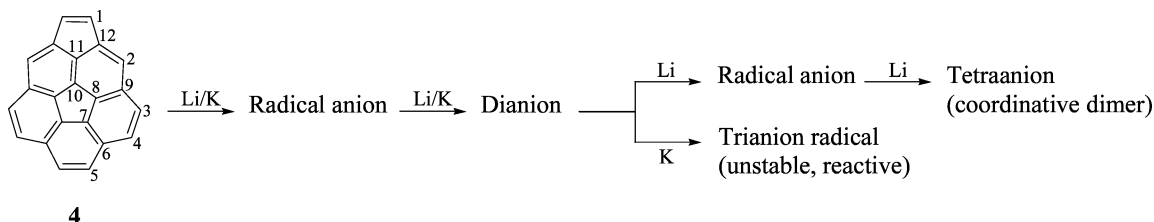
solubility of the dimer with lithium compared to potassium may arise from the different interactions that these cations have with the anionic moieties. The third reduction step is the trianion radical that undergoes irreversible reactions (e.g., solvation, protonation) at carbon atom C3, where the majority of the charge is concentrated.<sup>9b</sup> Most probably, the small lithium cation cannot stabilize the charge concentrated on carbon atom C3, leaving it very reactive.

The  $^1\text{H}$  NMR spectrum of the dianion with lithium ( $[\text{2}^{2-}/2\text{Li}^+]$ ) is very similar to that of the dianion with potassium ( $[\text{2}^{2-}/2\text{K}^+]$ ), which indicates that the cation has little effect on this reduction

## SCHEME 4



## SCHEME 5



stage. The corannulene rim protons are shifted to higher field than those on the benzene ring of the indeno-subunit. This means that the electrons are concentrated more on the corannulene subunit, and hence, the protons attached there are more affected by the paratropicity of the system.

The  $K_C$  values for  $2^{2-}/2Li^+$  and  $2^{2-}/2K^+$  are 63.8 and 65.2 ppm/electron, respectively, which shows that there is substantial anisotropy in the system.<sup>11</sup> This makes the calculation of the charge distribution using eq 1 unreliable because the carbon chemical shifts are not affected solely by the added charge. The high field shift of carbon atom C3 in both  $2^{2-}/2Li^+$  and  $2^{2-}/2K^+$  ( $\delta = 107.12$  and  $107.72$  ppm, respectively) shows that most of the charge resides there,<sup>27</sup> which is in line with the calculated atomic coefficients of the LUMO of **2**.<sup>9b</sup>

The tetraanion of **2** was obtained only with potassium ( $2^{4-}/4K^+$ ), and the calculated  $K_C$  value (118.1 ppm/electron) showed that anisotropy hardly affects the carbon absorptions. The charge distribution estimated from the  $^{13}C$  NMR spectrum shows that most of the charge is concentrated on carbon atoms C3, C4, and C14, in that order. The annulene-within-an-annulene model is not relevant in  $2^{4-}/4K^+$  as the  $^1H$  NMR chemical shifts are at a relatively high field for an aromatic system. This means that  $2^{4-}/4K^+$  is more polycyclic than annulenic in character. The high-field shift of protons H1, H4 and H3 results from the concentration of charge on their respective carbons.

**Diindenof[1,2,3-*bc*:1,2,3-*hi*]corannulene (3).** This compound was reduced with potassium, and three successive reduction steps were observed (Scheme 4). Further reduction to the tetraanion could not be achieved. The radical anion and trianion radical did not undergo reductive dimerization or any other reaction during reduction.

The  $^1H$  NMR chemical shifts and low  $K_C$  value (78.2 ppm/electron) of the dianion of **3** ( $3^{2-}/2K^+$ ) show that it is a paratropic system.<sup>11</sup> Judging from the chemical shifts of protons H6 and H7 ( $\delta = 5.78$  and  $5.72$  ppm, respectively), only the corannulene subunit has acquired anti-aromatic character, as the indeno-subunit benzene proton signals appear at lower field (aromatic region). The relatively low field shift of proton H1 ( $\delta = 7.16$  ppm) that resides on the corannulene rim results from its position in a bay region.

(27) The charge distribution for these dianions was calculated using another equation (ref 11) that takes into account the anisotropy effect, and it was found that most of the charge resides on carbon atom C3.

The anisotropy effect makes it difficult to correctly assess the charge distribution from the  $^{13}C$  NMR chemical shifts. Contrary to the behavior of **2**, no reductive dimerization was observed during the reduction of **3**. Thus, the addition of a second indeno subunit drastically alters the charge distribution in the system relative to that in **2**. This change prevents the concentration of spin density on any of the carbon atoms, so no dimerization occurs.

**Cyclopenta[*bc*]corannulene (4).** Compound **4** was reduced with lithium and potassium metals, and no reactions of the radical anion were observed with either metal. Moreover, it was found that beyond the dianion, the reduction process is alkali metal dependent (Scheme 5).

The lithium and potassium dianions of **4** ( $4^{2-}/2Li^+$  and  $4^{2-}/2K^+$ , respectively) exhibit almost identical NMR spectra. However, there is an interesting influence of the metal on the chemical shift of carbon atom C1. This carbon signal is shifted to a higher field by  $\Delta\delta_C = 13.03$  ppm in  $4^{2-}/2Li^+$  relative to that in  $4^{2-}/2K^+$ , indicating that more charge is concentrated on C1 in  $4^{2-}/2Li^+$  than in  $4^{2-}/2K^+$ . The difference could result from a stronger interaction of the lithium cation with the specific carbon atoms. Such an interaction would concentrate more charge on carbon atom C1 and hence shift its nuclear resonance to higher field.

The concentration of charge on carbon atom C1 also affects the  $^1H$  NMR spectrum. It can be seen that, except for proton H1, all the other protons of  $4^{2-}/2K^+$  are shifted to higher field than in  $4^{2-}/2Li^+$  ( $\Delta\delta_{avg} = 0.25$  ppm). Because more charge is found on the corannulene subunit of  $4^{2-}/2K^+$ , the anti-aromaticity of this system increases relative to that in  $4^{2-}/2Li^+$ . The  $K_C$  values calculated for both  $4^{2-}/2Li^+$  and  $4^{2-}/2K^+$  (89.9 and 76.8 ppm/electron, respectively) support this conclusion.

Further reduction of  $4^{2-}$  with potassium leads to the trianion radical, which is very reactive and undergoes further reactions (solvent cleavage, deuteration, etc.). The reduction with potassium stops at this step (Scheme 5).

With lithium as the reducing agent, a completely different and unprecedented behavior is observed. When  $4^{2-}$  is further reduced with lithium, the tetraanion ( $4^{4-}/4Li^+$ ) is obtained, which builds up as  $4^{2-}/2Li^+$  disappears (Scheme 5). The  $^1H$  NMR of  $4^{4-}/4Li^+$  shows that most of the peaks are shifted to high field, especially proton H2 ( $\delta = 2.51$  ppm). The NMR signal for carbon atom C2 is also shifted to very high field ( $\delta$

= 48.35 ppm), and its  $^1J_{\text{C,H}}$  coupling constant ( $^1J_{\text{C,H}} = 129.56$  Hz) indicates that it has become  $\text{sp}^3$ -hybridized. These data are reminiscent of the reductive dimerization observed in **2**;<sup>9b</sup> however, this time the rehybridization is not accompanied by symmetry loss.

In addition, the  $^7\text{Li}$  NMR spectra of  $4^{4-}$  offer compelling evidence for an aggregation process at this stage. The spectrum at 200 K consists of four main peaks that appear around  $\delta = -0.18$ ,  $-7.61$ ,  $-9.50$ , and  $-10.10$  ppm. The highly shifted lithium absorptions ( $\delta = -9.50$  and  $-10.10$  ppm) are diagnostic for strongly shielded lithium cations sandwiched between aromatic anionic layers.<sup>8</sup>

These results show that **4** yields both rehybridization of two specific carbon atoms and a layered anionic aggregate in its tetraanionic state.<sup>28</sup> This is reasonable as **4** can combine the characteristics of both **1** and **2** because it is structurally related to both. The formation of a layered compound is possible if the two C2 carbons of one unit of  $4^{4-}$  are connected with the corresponding C2 carbons of another. In this structure, the highly shifted lithium cations are “trapped” between two  $4^{4-}$  layers. The symmetry of the system indicates that the two units of  $4^{4-}$  are connected to each other via their convex faces.<sup>29</sup>

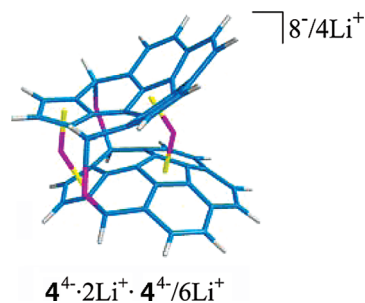
One explanation for the rehybridization of carbon atoms C2 in  $4^{4-}$  would be a reductive dimerization process involving C–C bond formation that takes place simultaneously at both C2 carbons, which could also explain why the  $C_s$  symmetry of the system is not lowered. However, the NMR data clearly show that this is not the case. First, no  $^3J_{\text{H}_2, \text{H}_2}$  coupling was observed for this new anionic molecule. This does not rigorously eliminate the presence of  $\sigma$ -bonds connecting the C2 carbons together, since the magnitude of this coupling is dependent on the dihedral angle between hydrogen atoms H2. The high symmetry observed in the  $^1\text{H}$  NMR spectrum, however, indicates that this angle is very close to zero degrees, and so the coupling expected for a direct C–C linkage should be observed using NMR. A second important interaction is also missing in the observed aggregate of  $4^{4-}$  a long-range correlation in the HMBC experiments between carbon atom C2 and proton H2 ( $^2J_{\text{C}_2, \text{H}_2}$  coupling). This coupling was observed in all previous reductive dimerization cases studied in our group,<sup>9b–e</sup> and even in a system that did not show  $^3J_{\text{H}, \text{H}}$  couplings.<sup>9e</sup> The absence of these couplings indicates that the rehybridization does not result from the formation of new C–C bonds.<sup>30</sup>

The most plausible explanation is lithiation, i.e., formation of C–Li–C bonds. The concentration of high charge density on carbon atoms C2 can induce a strong interaction with the lithium cations, which in turn can interact with the C2 carbons of another molecule, yielding a coordinative dimer (Figure 3,  $4^{4-} \cdot 2\text{Li}^+ \cdot 4^{4-}/6\text{Li}^+$ ). Such a dimer can explain the observed NMR spectra, the rehybridization of carbon atom C2 and the absence of the above-mentioned coupling constants. The ability of lithium cations to interact with numerous carbanionic centers has been extensively studied;<sup>31</sup> however, such a coordinative dimerization of a PAH has never been observed previously.<sup>32</sup>

(28) Solvent cleavage, deuteration or protonation cannot explain the observed phenomena and therefore they are not taken into consideration.

(29) A concave–convex interaction is excluded, as this would lower the symmetry of the system (duplicated signals in both  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra would be observed). Moreover, a fast bowl-to-bowl inversion (on the NMR time-scale) is not reasonable for such a system, and therefore, the high-symmetry cannot be due to an averaging of the signals.

(30) According to calculations (B3LYP/6-31G\*) carbon atom C2 in  $4^{4-}$  (monomer) resonates at  $\delta = 64.1$  ppm. This unusual high field shift for an  $\text{sp}^2$ -hybridized carbon stems from the concentration of high charge on it.



**FIGURE 3.** Calculated structure (PM3) of the coordinative dimer,  $4^{4-} \cdot 2\text{Li}^+ \cdot 4^{4-}/6\text{Li}^+$ . Such a structure conforms to the NMR data, as far as symmetry and the number of high field shifted lithium cations (in pink) are concerned.

One way of proving the existence of C–Li–C bonds would be to measure the  $^1J_{^{13}\text{C}, ^6\text{Li}}$  coupling that such a bond would yield.<sup>32</sup> For this purpose a sample of **4** was reduced using lithium[6]; however, the recorded spectra ( $^6\text{Li}$  and  $^{13}\text{C}$  NMR) did not show any such couplings, probably due to the broadness of the peaks.<sup>33</sup> Temperature dependent  $^{13}\text{C}$  NMR spectra were also measured, and it was found that the chemical shift of carbon atom C2 is not dependent on the temperature. This shows that the lithium cations do not change their ion pairing easily, supporting the proposed structure of the dimer,  $4^{4-} \cdot 2\text{Li}^+ \cdot 4^{4-}/6\text{Li}^+$  (Figure 3).

Further evidence for the formation of the coordinative dimer comes from self-diffusion experiments.<sup>34</sup> These experiments show that  $4^{4-} \cdot 2\text{Li}^+ \cdot 4^{4-}/6\text{Li}^+$  and  $1^{4-}/1^{4-}/8\text{Li}^+$  diffuse at similar rates in solution ( $D_{255,7\text{K}} = 2.5 \pm 0.1$  and  $2.44 \pm 0.04 \times 10^{-10}$   $\text{m}^2/\text{s}$ , respectively). Such behavior is expected if these two systems have similar sizes and charges in solution.

The reason this process is observed with lithium and not potassium stems from the fact that the lithium cations are smaller and can interact with and better stabilize the charge localized on carbon atom C2. The effect of counterion stabilization is already visible in the tri-anion radical where reactions occur with the potassium counterion.

An accurate charge distribution and  $K_C$  value cannot be calculated for  $4^{4-} \cdot 2\text{Li}^+ \cdot 4^{4-}/6\text{Li}^+$  because the reduction is accompanied by rehybridization.<sup>10</sup>

**Naphtho[2,3-*a*]corannulene (5).** The reduction of **5** with lithium and potassium stops at the trianion radical state (Scheme 6). Broad proton peaks are seen in the  $^1\text{H}$  NMR spectrum of the dianions ( $5^{2-}/2\text{Li}^+$  and  $5^{2-}/2\text{K}^+$ ) presumably due to singlet–triplet equilibrium. Neither the anion radical nor the trianion radical undergo any chemical reactions.

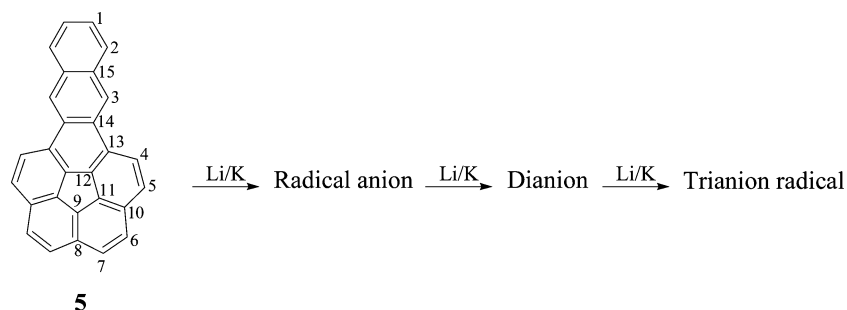
(31) For example: (a) Schuber, U.; Neugebauer, W.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1982**, 1184–1185. (b) Seebach, D.; Hässig, R.; Gabriel, J. *Helv. Chim. Acta* **1983**, *66*, 308–337. (c) Benken, R.; Werner, A.; Günther, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1182–1183. (d) Bauer, W.; O’Doherty, G. A.; Schleyer, P. v. R.; Paquette, L. A. *J. Am. Chem. Soc.* **1991**, *113*, 7093–7100. (e) Sekiguchi, A.; Ichinohe, M.; Nakanishi, T.; Kabuto C.; Sakurai, H. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 3215–3220.

(32) For an example of a lithium cation binding two carbanionic centers see, Böhrer, B.; Hüls, D.; Günther, H. *Tetrahedron Lett.* **1996**, *37*, 8719–8722.

(33) According to literature the  $^1J_{^{13}\text{C}, ^6\text{Li}}$  coupling is highly dependent on temperature and degree of aggregation. For dimers (not PAHs) values of 2–3 Hz were observed, whereas monomers can give couplings of up to 17 Hz. Moreover, these couplings cannot be observed above ca. 200 K. See: Günther, H. *J. Braz. Chem. Soc.* **1999**, *10*, 241–262 and references therein.

(34) Cohen, Y.; Avram, L.; Frish, L.; *Angew. Chem., Int. Ed.* **2005**, *44*, 520–554 and references therein.

## SCHEME 6



**TABLE 1.** Calculated  $K_C$  Values (ppm/Electron) for the Observed Dianions and Tetraanions of 1–7

	1 <sup>a</sup>	2	3	4	5	6 <sup>b</sup>	7 <sup>b</sup>
dianion:							
lithium	-182.5	63.8	<i>c</i>	89.9	-21.1	-25.0	89.0
potassium	-178.5	65.2	78.2	76.8	-23.0	-25.0	80.0
tetraanion:							
lithium	179.8	<i>d</i>	<i>c</i>	101.7	<i>d</i>	<i>d</i>	<i>d</i>
potassium	141.9	118.1	<i>e</i>	<i>e</i>	<i>e</i>	<i>f</i>	<i>f</i>

<sup>a</sup> Data taken from ref 18c,f. <sup>b</sup> Data taken from ref 24. <sup>c</sup> Not reduced with lithium. <sup>d</sup> Tetraanion not observed with lithium. <sup>e</sup> Tetraanion not observed with potassium. <sup>f</sup> Data not reported.

The high field shift of the protons of both  $5^{2-}/2Li^+$  and  $5^{2-}/2K^+$  shows that the dianions have substantial anti-aromatic character. This is also indicated by the unusually low  $K_C$  values calculated for  $5^{2-}/2Li^+$  and  $5^{2-}/2K^+$ , -21.5 and -23.0 ppm/electron, respectively.<sup>11</sup>

The different cations cause a slight difference in the <sup>1</sup>H NMR chemical shifts. The signals for protons H1, H2 and H3 that belong to the naphthalene subunit are shifted to higher field by  $\Delta\delta_{avg} = 1.19$  ppm in  $5^{2-}/2Li^+$  relative to those in  $5^{2-}/2K^+$ , which indicates that the naphthalene ring in  $5^{2-}/2Li^+$  is more paratropic than in  $5^{2-}/2K^+$ . This can result from a stronger interaction of the lithium cation with the naphtho group, which can in turn withdraw more electrons to this subgroup, making it more anti-aromatic. On the other hand more charge is found in the corannulene core of  $5^{2-}/2K^+$  compared to  $5^{2-}/2Li^+$ , making it more anti-aromatic. This is evident from the higher field shifts of the corannulene rim protons of  $5^{2-}/2K^+$  ( $\Delta\delta_{avg} = 0.64$  ppm).<sup>35</sup>

In these dianions as well, an accurate charge distribution cannot be obtained from NMR because of the anisotropy in the system.<sup>11</sup>

**A General View.** For a better understanding of the reduction of **1** and its derivatives (**2**–**5**), it is informative to compare their reduction processes, especially their charge distributions,  $K_C$  values and reduction states (Table 1). To further clarify the picture, the comparison also includes the reduction results of **6**,<sup>24</sup> and **7**.<sup>24</sup>

**Dianions:** The dianion of **1** is anti-aromatic and has a very negative  $K_C$  value (-182.5 and -178.5 ppm/electron for  $1^{2-}/2Li^+$  and  $1^{2-}/2K^+$ , respectively) despite the added charge. These negative  $K_C$  values deviate drastically from the norm<sup>10</sup> and result from the annulenic behavior of **1**. Although negative charge is added, the hub carbons in  $1^{2-}$  are shifted to very low field because they are affected by the paratropic magnetic field induced by the rim carbons. Deviation from such a negative

$K_C$  value in the dianion will mean that the system is less annulenic. Thus, the  $K_C$  value can be used to scale the annulenic behavior of the dianions of the derivatives of **1**.

The  $K_C$  values of the dianions clearly show the effect of annelation on the reduction of **1** (Table 1). It can be seen that annelation with a 6MR (**5** and **6**) yields paratropic dianions; however, the degree of paratropicity is much lower than in  $1^{2-}$ . The lower symmetry and enlargement of the  $\pi$ -system lowers the anti-aromatic character by altering the charge distribution, and the compounds start behaving more like polycyclic compounds (Table 1).

The effect of *peri*-annelation with a 5MR is much greater. It can be seen that the  $K_C$  values of the dianions **2**–**4** are positive; however, they are still less than the normal value of  $K_C$ .<sup>11</sup> This means that there are still anisotropy effects in these compounds, but they are far less significant than in  $1^{2-}$ . The reason for this is that the 5MR functions as an electron-withdrawing group and drastically alters the charge distribution found in **1**. The anisotropy makes it difficult to obtain accurate charge distributions; therefore, it is not possible to assess how much of the charge is concentrated in the 5MRs. A comparison between the  $K_C$  values of **4** and **7** shows that the 5MR and not the 6MRs is the decisive factor in altering the behavior of the dianions as their  $K_C$  values are quite similar.<sup>36</sup> The  $K_C$  values of the dianions obtained with potassium can be used to scale the annulenic character of these compounds (Table 1):  $1^{2-} \gg 6^{2-} \approx 5^{2-} > 2^{2-} > 4^{2-} \approx 3^{2-} \approx 7^{2-}$ .<sup>37</sup>

**Tetraanions:** The effect of the counterion, e.g.,  $Li^+$  or  $K^+$ , is very clear in the tetraanionic state. It can be seen that most of the annelated compounds do not yield tetraanions with lithium, with the only exception being **4**. This can be explained in terms of a special type of anion stabilization. It seems that, without forming supramolecular dimers, the lithium cations cannot efficiently stabilize the high charge density on these large compounds. These annelated corannulenes cannot form dimers as **1** does because the charge distribution has been altered and not enough charge can be concentrated on the corannulene

(36) One of the samples of **4** contained some traces of the saturated compound (**4**·2H) that also got reduced to a dianion (**4**·2H<sup>2-</sup>/2Li<sup>+</sup>). The center of gravity of the <sup>1</sup>H NMR spectrum in **4**·2H<sup>2-</sup>/2Li<sup>+</sup> is  $\delta_{center} = 1.02$  ppm, whereas the center of gravity for **4**<sup>2-</sup> is  $\delta_{center} = 6.06$  and 5.90 ppm for **4**<sup>2-</sup>/2Li<sup>+</sup> and **4**<sup>2-</sup>/2K<sup>+</sup>, respectively. The difference between **4**<sup>2-</sup> and **4**·2H<sup>2-</sup>/2Li<sup>+</sup> shows the influence that a single double bond has over the reduced compound. Whereas **4**<sup>2-</sup> is mildly paratropic and more polycyclic in behavior, **4**·2H<sup>2-</sup>/2Li<sup>+</sup> is strongly paratropic and annulenic in behavior.

(37) A partial scale can also be made for the lithium reduced compounds:  $1^{2-} \gg 6^{2-} \approx 5^{2-} > 2^{2-} > 7^{2-} \approx 4^{2-}$ . The effect of the alkali metal can also be seen in this scale as the order in which **7**<sup>2-</sup> and **4**<sup>2-</sup> appear with lithium as counterion, is reversed from that of potassium.

(38) (a) Scott, L. T.; Bratcher, M. S.; Hagen, S. *J. Am. Chem. Soc.* **1996**, *118*, 8743–8744. (b) Necula, A.; Scott, L. T. *J. Anal. Appl. Pyrolysis* **2000**, *54*, 65–87.

(35) Proton H14 is found in the bay area; therefore, its chemical shift was not taken into consideration when calculating the average proton shift.

subunit. On the other hand, the potassium cation is larger and can stabilize these multicharged systems, and therefore, it yields the tetraanions.

The reduction of **2** with potassium and lithium shows another important facet of counterion stabilization. Two successive reductive dimerization processes were observed while reducing **2** to its tetraanion with potassium. This was possible because the radical anions were stabilized by the counterion. However, lithium yielded only one covalent dimer; its cations did not stabilize the trianion radical of **2**, so it reacted differently.

The importance of counterion stabilization is encountered again in the reduction of **4** to its tetraanion. This is possible only with lithium as it forms a layered compound similar to **1**<sup>4-</sup>. However, this time the cations hold the layers together by forming bonds with carbon atoms C2. The formation of this coordinative dimer enables the reduction of **4** to a tetraanion, as it can stabilize the resulting anionic system. The inability of potassium cations to stabilize the trianion radical prevents potassium from reducing **4** to a tetraanion.

## Conclusions

This study shows that the reduction of corannulene derivatives yields different results depending on both the type of the derivative and the reducing metal. It has also been shown that formation of a supramolecular dimer is not the only fascinating process that such derivatives can undergo.

A new type of coordinative dimer was observed for **4**<sup>4-</sup>, which combines the characteristics of the already known supramolecular dimer of **1**<sup>4-</sup> and the covalent dimers of **2**. The two anionic layers that constitute this new dimer are held together by C–Li–C bonds and contain lithium cations trapped between them.

It was shown that annelation of **1** with 6MRs and 5MRs strongly affects the reduction process and its outcome. When corannulene is annelated with a 6MR, the annulenic behavior and anti-aromatic character of the dianion is significantly diminished relative to that in **1**<sup>2-</sup>. However, the effect is less pronounced than in compounds that are *peri*-annelated with 5MRs. This means that compounds with 5MRs behave more as polycyclic systems rather than as annulenic ones.

It is now evident that the reduction of corannulene or its annelated derivatives to tetraanions with lithium requires special stabilizing effects, as the lithium cations cannot stabilize the large anions by themselves. The stabilizing effect can be either the formation of supramolecular dimers, as is the case in **1**, or the formation of a coordinative dimer, as in **4**. In the other instances, **2**, **5**, **6**, and **7**, the reduction with lithium stopped at the trianion radical, and no tetraanion was formed.

On the other hand more tetraanions are formed when potassium is used as the reducing metal. This is due to the ability of the potassium cations to stabilize the large anionic systems.

## Experimental Section

For general methods, see the Supporting Information.

**NMR Data.** **2**, [2–2]<sup>n-</sup>/nK<sup>+</sup> (*n* = 2, 6), 2<sup>2-</sup>/2K<sup>+</sup>, and 2<sup>4-</sup>/4K<sup>+</sup>: The <sup>1</sup>H and <sup>13</sup>C NMR spectra of these compounds were reported in ref 9b.

[2–2]<sup>2-</sup>/2Li<sup>+</sup>: <sup>1</sup>H NMR (THF-*d*<sub>8</sub>, 240 K) δ 7.77 (s, 1H, H3), 7.74 (d, 1H, <sup>3</sup>J<sub>H,H</sub> = 7.12 Hz, H2), 7.34 (d, 1H, <sup>3</sup>J<sub>H,H</sub> = 8.56 Hz, H4), 7.17–7.14 (m, 3H, H4', H5, H5'), 7.03 (s, 2H, H6, H6'), 6.78 (d, 1H, <sup>3</sup>J<sub>H,H</sub> = 8.81 Hz, H2'), 6.70 (dd, 1H, <sup>3</sup>J<sub>H,H</sub> = 7.05, 8.56 Hz, H1'), 6.30 (dd, 1H, <sup>3</sup>J<sub>H,H</sub> = 7.05, 7.55 Hz, H1), 5.45 (s, 1H, H3').

The <sup>1</sup>H NMR was assigned according to the signals of 2–2<sup>2-</sup>/2K<sup>+</sup>. It was not possible to measure the <sup>13</sup>C NMR spectrum due to the low solubility.

2<sup>2-</sup>/2Li<sup>+</sup>: <sup>1</sup>H NMR (THF-*d*<sub>8</sub>, 200 K) δ<sub>H</sub> = 7.83 (m, 1H, H2), 6.83 (m, 1H, H1), 5.58 (d, 1H, <sup>3</sup>J<sub>H,H</sub> = 9.57 Hz, H4), 5.38 (s, 1H, H3), 5.31 (d, 1H, <sup>3</sup>J<sub>H,H</sub> = 9.47 Hz, H5), 4.95 (s, 1H, H6); <sup>13</sup>C NMR (THF-*d*<sub>8</sub>, 200 K) δ 163.7 (C10), 157.1 (C8), 141.6 (C9), 140.2 (C12), 134.5 (C11), 133.0 (C14), 132.4 (C7), 131.5 (C4), 126.2 (C5), 118.2 (C2), 115.4 (C13), 112.6 (C6), 108.1 (C1), 107.1 (C3); <sup>7</sup>Li NMR (THF-*d*<sub>8</sub>, 220 K) δ –0.15, –1.18.

**3: Synthesis. A. 1,5-Bis-(2-bromobenzoyl)corannulene (8) and 1,8-Bis-(2-bromobenzoyl)corannulene (9).** To a room-temperature solution of 2-bromobenzoyl chloride (180 mg, 0.820 mmol) in 20 mL of methylene chloride was added aluminum chloride (220 mg, 1.65 mmol). After 15 min of stirring at room temperature, corannulene (100 mg, 0.400 mmol) in 20 mL of methylene chloride was added, and the reaction mixture was stirred at room temperature for 3 h. The reaction was quenched by pouring the flask contents into ice–water/hydrochloric acid (1:1), and the mixture was extracted with methylene chloride (3 × 50 mL). The combined organic layers were dried over magnesium sulfate, filtered, and concentrated to dryness under reduced pressure to afford 234 mg of a yellow solid. The crude product consists of a mixture of the isomeric ketones **8** and **9** in the approximate ratio of **8**/**9** = 3:2, as determined by <sup>1</sup>H NMR analysis. The combined yield of the two isomers was ca. 95%. All attempts to isolate pure samples of compounds **8** and **9** were unsuccessful; however, enriched samples of compound **9** could be obtained: HRMS calcd for C<sub>34</sub>H<sub>16</sub>Br<sub>2</sub>O<sub>2</sub> 613.9517, found 613.9520.

**8:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.67 (d, <sup>3</sup>J<sub>H,H</sub> = 8.8 Hz, 1H), 8.62 (d, <sup>3</sup>J<sub>H,H</sub> = 8.8 Hz, 1H), 8.11 (s, 1H), 8.09 (s, 1H), 7.92–7.70 (m, 6H), 7.54–7.41 (m, 6H).

**9:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.63 (s, 2H), 8.12 (s, 2H), 7.92–7.70 (m, 6H), 7.54–7.41 (m, 6H).

**B. Diindeno[1,2,3-*bc*:1,2,3-*hi*]corannulene (3) and Diindeno[1,2,3-*bc*:1,2,3-*ef*]corannulene (10).** A 50 mg sample of the bis-(2-bromobenzoyl)corannulene prepared as above (isomer ratio **8**/**9** = ca. 3:2) was pyrolyzed at 1100 °C with a steady flow of nitrogen carrier gas (final pressure 1.8–2.0 mmHg) as previously described.<sup>26,38</sup> The crude pyrolysate (16 mg, mass recovery 50%) was analyzed by <sup>1</sup>H NMR spectroscopy, which revealed the presence of **3** (38%), **10** (5%), and indeno[1,2,3-*bc*]corannulene (**2**) (57%), along with trace amounts of corannulene and keto-byproducts. Separation by preparative thin-layer chromatography on silica gel with cyclohexane as eluant afforded a small sample (2.5 mg, yield 7.7%) of pure **3**: mp 267–268 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.64–7.58 (m, 4H), 7.53 (s, 2H), 7.47 (s, 2H), 7.45 (s, 2H), 7.21–7.18 (m, 4H); <sup>13</sup>C NMR: the acquisition was precluded by aggregation and poor solubility; UV–vis λ<sub>max</sub> (rel intensity) (CHCl<sub>3</sub>) 250 (sh, 0.887), 260 (sh, 0.951), 276 (1.080), 332 (0.585), 350 (sh, 0.445); HRMS calcd for C<sub>32</sub>H<sub>14</sub> 398.1095, found 398.1097.

**10:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.68–7.58 (m, 4H), 7.48 (s, 2H), 7.43 (d, <sup>3</sup>J<sub>H,H</sub> = 8.4 Hz, 2H), 7.31 (d, <sup>3</sup>J<sub>H,H</sub> = 8.4 Hz, 2H), 7.21–7.18 (m, 4H).

**3:** <sup>1</sup>H NMR (THF-*d*<sub>8</sub>, 273 K) δ 7.67 (s, 1H, H1), 7.64–7.68 (m, 2H, H5 and H2), 7.58 (s, 1H, H6), 7.54 (s, 1H, H7), 7.17–7.21 (m, 2H, H3 and H4); <sup>13</sup>C NMR (THF-*d*<sub>8</sub>, 273 K) δ 145.6 (C12), 143.3 (C14), 142.3 (C13), 141.9 (C15), 141.5 (C11), 140.4 (C17, C10), 140.1 (C16), 139.7 (C9), 137.2 (C8), 129.3 (C3), 129.3 (C4), 129.2 (C7), 124.9 (C1), 123.1 (C6), 122.5 (C5) 122.3 (C2).

3<sup>2-</sup>/2K<sup>+</sup>: <sup>1</sup>H NMR (THF-*d*<sub>8</sub>, 200 K) δ 7.97 (d, 1H, <sup>3</sup>J<sub>H,H</sub> = 7.67 Hz, H2), 7.63 (d, 1H, <sup>3</sup>J<sub>H,H</sub> = 7.81 Hz, H5), 7.16 (s, H1), 7.12 (dd, 1H, <sup>3</sup>J<sub>H,H</sub> = 7.29, 7.34 Hz, H4), 6.95 (dd, 1H, <sup>3</sup>J<sub>H,H</sub> = 7.30, 7.20 Hz, H3), 5.78 (s, 1H, H6), 5.72 (s, 1H, H7); <sup>13</sup>C NMR (THF-*d*<sub>8</sub>, 273 K) δ 161.0 (C12), 156.0 (C9), 139.7 (C16), 137.2 (C14), 136.5 (C11), 134.9 (C17), 134.5 (C8), 132.0 (C10), 130.6 (7), 128.6 (C13), 125.1 (C1), 120.5 (C15), 120.4 (C2), 119.2 (C4), 118.5 (C5), 114.6 (C3), 110.7 (C6).



**4:**  $^1\text{H}$  NMR (THF- $d_8$ , 298 K)  $\delta$  7.53 (d, 1H,  $^3J_{\text{H,H}} = 8.83$  Hz, H3), 7.46 (d, 1H,  $^3J_{\text{H,H}} = 8.83$  Hz, H4), 7.39 (s, 1H, H5), 7.35 (s, 1H, H2), 5.50 (s, 1H, H1);  $^{13}\text{C}$  NMR (THF- $d_8$ , 298 K)  $\delta$  145.2 (C12), 144.9 (C11), 140.2 (C10), 138.9 (C8), 138.8 (C9), 138.7 (C7), 131.0 (C6), 129.2 (C1, C3), 128.1 (C5), 127.3 (C4), 125.0 (C2).

$4^{2-}/2\text{Li}^+$ :  $^1\text{H}$  NMR (THF- $d_8$ , 200 K)  $\delta$  6.38 (d, 1H,  $^3J_{\text{H,H}} = 9.14$  Hz, H3), 6.33 (d, 1H,  $^3J_{\text{H,H}} = 9.05$  Hz, H4), 6.06 (s, 1H, H5), 5.98 (s, 1H, H1), 5.55 (s, 1H, H2);  $^{13}\text{C}$  NMR (THF- $d_8$ , 200 K)  $\delta$  154.8 (C10), 149.7 (C7), 137.2 (C9), 131.8 (C8), 130.0 (C3), 128.7 (C6, C11), 126.7 (C4), 126.6 (C12), 113.6 (C5), 103.3 (C2), 94.7 (C1);  $^7\text{Li}$  NMR (THF- $d_8$ , 200 K)  $\delta = -0.31$  ppm.

$4^{2-}/2\text{K}^+$ :  $^1\text{H}$  NMR (THF- $d_8$ , 200 K)  $\delta$  6.19 (s, 1H, H1), 6.10 (broad, 2H, H3, H4), 5.84 (s, 1H, H5), 5.27 (s, 1H, H2);  $^{13}\text{C}$  NMR (THF- $d_8$ , 200 K)  $\delta$  157.8 (C10), 150.9 (C7), 134.5 (C9), 131.0 (C8), 130.4 (C11), 130.1 (C3), 128.4 (C6), 127.2 (C4), 124.7 (C12), 113.5 (C5), 107.7 (C1), 105.1 (C2).

$4^{4-}/2\text{Li}^+ \cdot 4^{4-}/6\text{Li}^+$ :  $^1\text{H}$  NMR (THF- $d_8$ , 250 K)  $\delta$  6.53 (s, 1H, H5), 6.11 (d, 1H,  $^3J_{\text{H,H}} = 7.38$  Hz, H4), 5.91 (d, 1H,  $^3J_{\text{H,H}} = 7.34$  Hz, H3), 4.38 (s, 1H, H1), 2.52 (s, 1H, H2);  $^{13}\text{C}$  NMR (THF- $d_8$ , 250 K)  $\delta$  152.5 (C9), 150.9 (C8), 135.5 (C7), 127.4 (C6), 122.3 (C5), 122.7 (C12), 114.8 (C3), 113.2 (C4), 109.8 (C11), 94.1 (C10), 81.1 (C1), 48.3 ( $^1J_{\text{C,H}} = 129.56$ , C2);  $^7\text{Li}$  NMR (THF- $d_8$ , 180 K)  $\delta -0.18, -7.61, -9.50$  and  $-10.10$ .

**5: Synthesis. A. (2-Carboxybenzoyl)corannulene (11).** A mixture of phthalic anhydride (18 mg, 0.12 mmol) and aluminum chloride (50 mg, 0.37 mmol) in 2 mL of methylene chloride was stirred at room temperature for 15 min. To the stirring suspension was added slowly a solution of corannulene (25 mg, 0.1 mmol) in 5 mL of methylene chloride, and the resulting mixture was stirred at room temperature for 20 h. The reaction was quenched by pouring the flask contents into hydrochloric acid/water 1:1, and the mixture was extracted with methylene chloride (3  $\times$  30 mL). The combined organic layer were washed with water (2  $\times$  40 mL) and dried over anhydrous magnesium sulfate. The solvent was evaporated under reduced pressure to afford the crude product as a brown solid. Column chromatography on silica gel with methylene chloride as eluent afforded some unreacted phthalic anhydride and a trace of corannulene. Further elution with acetonitrile afforded (2-carboxybenzoyl)corannulene (**11**) as an orange-brown solid (28 mg, 70% yield): mp 261–262  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.50 (d,  $^3J_{\text{H,H}} = 8.8$  Hz, 1H), 7.99 (d,  $^3J_{\text{H,H}} = 7.6$  Hz, 1H), 7.79 (s, 1H), 7.76–7.64 (m, 7H), 7.58–7.52 (m, 2H), 7.48 (d,  $^3J_{\text{H,H}} = 7.6$  Hz, 1H);  $^1\text{H}$  NMR (400 MHz, acetone- $d_6$ )  $\delta$  8.63 (d,  $^3J_{\text{H,H}} = 8.8$  Hz, 1H), 8.09 (d,  $^3J_{\text{H,H}} = 7.6$  Hz, 1H), 8.02 (d,  $^3J_{\text{H,H}} = 8.8$  Hz, 1H), 8.00 (bs, H), 7.95 (d,  $^3J_{\text{H,H}} = 8.8$  Hz, 1H), 7.93 (d,  $^3J_{\text{H,H}} = 8.8$  Hz, 1H), 7.88 (d,  $^3J_{\text{H,H}} = 8.8$  Hz, 1H), 7.84 (d,  $^3J_{\text{H,H}} = 7.2$  Hz, 1H), 7.76 (t,  $^3J_{\text{H,H}} = 7.6$  Hz, 1H), 7.71 (t,  $^3J_{\text{H,H}} = 7.6$  Hz, 1H);  $^{13}\text{C}$  NMR: the acquisition was precluded by aggregation and poor solubility; IR ( $\nu$ ,  $\text{cm}^{-1}$ ) 1703, 1659 (C=O groups); HRMS calcd for  $\text{C}_{28}\text{H}_{14}\text{O}_3$  398.0943, found 398.0946.

**B. Naphtho[2,3-*a*]corannulene (5).** A mixture of ketoacid **11** (40 mg, 0.1 mmol) and red phosphorus (200 mg) in a solution prepared from 5 mL of a 40% aqueous solution of hydroiodic acid

and 50 mL of glacial acetic acid was heated under reflux for 4 days. The flask contents were cooled to room temperature and filtered through a short pad of silica gel. The resulting solution was extracted with methylene chloride (3  $\times$  30 mL), and the pad of silica gel was washed with methylene chloride (ca. 100 mL). The combined organic layers were washed with 10% sodium hydroxide (3  $\times$  40 mL), 10% sodium thiosulfate (2  $\times$  30 mL), and water and then dried over anhydrous magnesium sulfate and filtered. The solvent was evaporated under reduced pressure. The crude product was separated by column chromatography on silica gel using pentane:methylene chloride 5:1 as eluent to afford 25.4 mg of naphtho[2,3-*a*]corannulene (**5**) as a yellow-orange solid (72% yield): mp 268–270  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.12 (s, 2H), 8.34 (d,  $^3J_{\text{H,H}} = 8.8$  Hz, 2H), 8.18 (m, 2H), 7.99 (d,  $^3J_{\text{H,H}} = 8.8$  Hz, 2H), 7.87 (d,  $^3J_{\text{H,H}} = 8.8$  Hz, 2H), 7.83 (d,  $^3J_{\text{H,H}} = 8.8$  Hz, 2H), 7.64 (m, 2H) (residual  $\text{CHCl}_3$  signal at 7.26 ppm used as reference);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  138.3, 135.7, 135.3, 132.3, 131.8, 130.9, 130.8, 129.4, 128.5, 127.9, 127.4, 127.2, 126.6, 124.5, 124.3; UV-vis  $\lambda_{\text{max}}$  ( $\epsilon$ ) ( $\text{CH}_2\text{Cl}_2$ ) 232 (3600), 280 (8000), 304 (5300), 394 (670), 374 (720), 406 (sh, 520); HRMS calcd for  $\text{C}_{28}\text{H}_{14}$  350.1095, found 350.1094.

**5:**  $^1\text{H}$  NMR (THF- $d_8$ , 200 K)  $\delta$  9.36 (s, H3), 8.53 (d, 1H,  $^3J_{\text{H,H}} = 8.64$  Hz, H4), 8.25 (m, 1H, H2), 8.08 (d, 1H,  $^3J_{\text{H,H}} = 8.63$  Hz, H5), 7.96 (d, 1H,  $^3J_{\text{H,H}} = 8.80$  Hz, H6), 7.92 (d, 1H,  $^3J_{\text{H,H}} = 8.69$  Hz, H7), 7.68 (m, 1H, H1);  $^{13}\text{C}$  NMR (THF- $d_8$ , 200 K)  $\delta$  138.7 (C9), 136.1 (C11), 135.6 (C12), 133.1 (C15), 132.2 (C14), 131.8 (C8), 131.7 (C10), 130.2 (C13), 129.5 (C2), 128.8 (C5), 128.2 (C6), 128.0 (C7), 127.4 (C1), 125.5 (C4), 125.3 (C3).

$5^{2-}/2\text{Li}^+$ :  $^1\text{H}$  NMR (THF- $d_8$ , 200 K)  $\delta$  4.36 (d, 1H,  $^3J_{\text{H,H}} = 7.69$  Hz, H7), 3.79 (m, 1H, H1), 3.72 (d, 1H,  $^3J_{\text{H,H}} = 7.56$  Hz, H6), 2.81 (m, 1H, H2), 2.57 (d, 1H,  $^3J_{\text{H,H}} = 6.61$  Hz, H5), 2.47 (d, 1H,  $^3J_{\text{H,H}} = 6.47$  Hz, H4), 1.20 (s, 1H, H1);  $^{13}\text{C}$  NMR (THF- $d_8$ , 200 K)  $\delta$  163.9 (C11), 151.8 (C15), 150.0 (C14), 148.4 (C12), 145.8 (C10), 140.3 (C9), 134.0 (C8), 125.5 (C13), 124.9 (C1), 123.8 (C7), 121.8 (C4), 120.2 (C2), 117.5 (C6), 110.1 (C3), 107.5 (C5);  $^7\text{Li}$  NMR (THF- $d_8$ , 200 K)  $\delta$  0.28.

$5^{2-}/2\text{K}^+$ :  $^1\text{H}$  NMR (THF- $d_8$ , 200 K)  $\delta$  4.85 (m, 1H, H1), 4.17 (m, 1H, H2), 3.69 (d, 1H,  $^3J_{\text{H,H}} = 8.04$  Hz, H7), 3.02 (d, 1H,  $^3J_{\text{H,H}} = 8.07$  Hz, H6), 2.50 (d, 1H,  $^3J_{\text{H,H}} = 7.24$  Hz, H4), 2.34 (s, 1H, H3), 2.02 (d, 1H,  $^3J_{\text{H,H}} = 7.26$  Hz, H5);  $^{13}\text{C}$  NMR (THF- $d_8$ , 200 K)  $\delta$  165.6 (C11), 151.7 (C12), 148.0 (C10), 147.2 (C14), 145.0 (C15), 142.1 (C9), 131.9 (C8), 125.6 (C1), 125.3 (C13), 125.0 (C7), 123.6 (C2), 121.4 (C4), 115.5 (C6), 113.7 (C3), 105.5 (C5).

**Acknowledgment.** This work was supported by the United States–Israel Binational Science Foundation (BSF) and the U.S. Department of Energy. I.A. is thankful for the Horowitz Foundation Scholarship.

**Supporting Information Available:** Experimental details, NMR spectra of compounds **3**, **5**, and **8–11** and the computational data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO051949C