Dianions and Tetraanions of Bowl-Shaped Fullerene Fragments Dibenzo[*a,g*]corannulene and Dibenzo[*a,g*]cyclopenta[*kl*]corannulene

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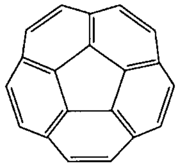
Abstract: The $C_{28}H_{14}$ and $C_{30}H_{14}$ polycyclic aromatic hydrocarbons dibenzo[*a,g*]corannulene (**3**) and dibenzo[*a,g*]cyclopenta[*kl*]corannulene (**4**) both contain a central corannulene ring system fused on two sides by benzene rings. Hydrocarbon **4** also has a second five-membered ring in the form of an etheno bridge on the corannulene. Two-electron reduction of these corannulene derivatives with lithium metal produces stable solutions of purple dianions that are amenable to study by ^1H, ^{13}C, and ^7Li NMR spectroscopy. The dianion of dibenzo[*a,g*]corannulene ($\mathbf{3}^{2-}$) is found to be paratropic, though less so than the dianion of the parent corannulene $\mathbf{1}^{2-}$, whereas the dianion of dibenzo[*a,g*]cyclopenta[*kl*]corannulene ($\mathbf{4}^{2-}$) is found to be diatropic. Analogous results were obtained when the two-electron reduction was carried out with potassium metal. Further reduction of the dianion with lithium metal gave the corresponding trianion radicals but, in contrast to the reduction of unsubstituted corannulene with lithium, could not be pushed beyond that stage to the tetraanions. However, with potassium metal, which reduces unsubstituted corannulene only to the trianion radical, both **3** and **4** could be reduced to tetraanions. The tetraanion of dibenzo[*a,g*]corannulene ($\mathbf{3}^{4-}$) was found to be diatropic, though less so than the tetraanion of corannulene ($\mathbf{1}^{4-}$), whereas the tetraanion of dibenzo[*a,g*]cyclopenta[*kl*]corannulene ($\mathbf{4}^{4-}$) was found to be weakly paratropic. The different π topologies, charge distributions, and magnetic properties of these two large fullerene fragments and their derived anions are discussed.

Keywords: annulenes · diatropism · magnetic properties · paratropism · ring currents

Introduction

Corannulene (**1**), with its bowl-shaped equilibrium geometry, represents the smallest subunit of C_{60} that retains a curved surface. The lowest unoccupied molecular orbital (LUMO) of corannulene lies unusually low in energy and is doubly degenerate; this accounts for the ease with which this $C_{20}H_{10}$ hydrocarbon can accept up to four electrons.[1] Renewed interest in the bowl-shaped corannulene following the discovery of C_{60} led to the development of a convenient new synthesis for corannulene and its derivatives[2] as well as to further investigation of their electronic and geometric structure.[3] Our discovery of the tetraanion $\mathbf{1}^{4-}$ on lithium reduction[1] and its dimerization[4] to **2** prompted further investigation of the various reduction states.[5] Attention turned to the nature of the dianion, being either para- or diatropic, since it had not been detected previously. We were also concerned with the question of the reduction stage in which the formation of dimers occurs.



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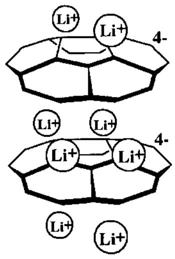

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Under the right conditions,[5] the dianion $\mathbf{1}^{2-}$ was observed by ^1H NMR spectroscopy, in the form of one line at $\delta = -5.6$.[5] This significant paratropic shift confirms its annulene nature.[4] A reduction path for corannulene was also suggested, indicating that the formation of the dimer takes place only at the tetraanionic stage of the reduction.[5]

The questions that arose from our work on the anions of corannulene (**1**) and other anions are: a) to what extent does

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aggregation occur in solvated organic anions, and b) does the reduction to polyanionic species promote the dimerization or vice versa? Corannulene (**1**) also behaves differently depending on whether it is reduced with lithium or potassium. With Li as the reducing metal it forms a tetraanionic sandwich compound **2**, but reduction with K yields the monomeric dianion with a minor quantity of a radical trianion, but no tetraanion, either as the monomer or the dimer. This has led us to study the reduction of extended corannulenes such as dibenzo[*a,g*]corannulene (**3**)[6] and dibenzo[*a,g*]cyclopenta[*kl*]corannulene (**4**),[7] which also have low-lying LUMOs and can, in principle, accept up to four electrons like corannulene (**1**). Both **3** and **4** are extended corannulenes with extra conjugated five- and/or six-membered rings. These are larger subunits of C_{60} with 28 and 30 carbon atoms, respectively, in which the bowl-type structure is maintained (Figure 1).

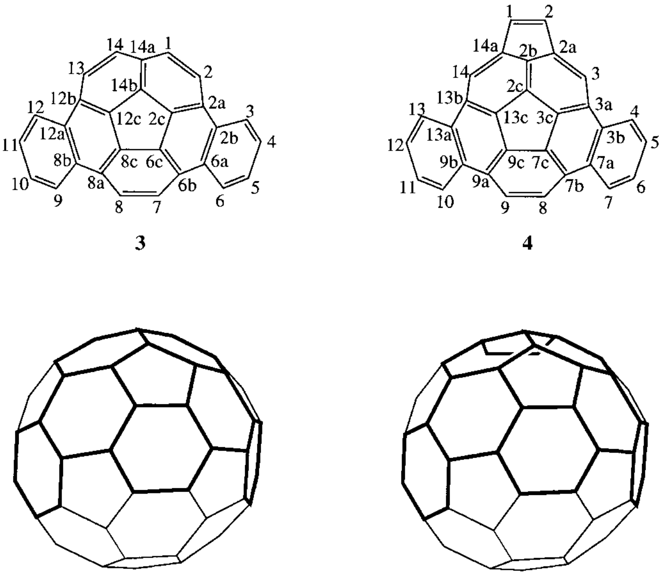


Figure 1. Corannulenes **3** and **4** and the relationship of their ring system to that of C_{60}.

We have used the same two alkali metals, lithium and potassium, for the reduction of **3** and **4**. The reduction process is followed by NMR spectroscopy in order to obtain information on the nature of the anions, for example the charge distribution and the magnetic properties of the ions. Here we describe our study of these two extended corannulenes **3** and **4**. The reduction products of these curved C_{60} subunits show a dependence on the reducing metal as well as on the π array of electrons. With lithium, **3** and **4** are reduced only to radical trianions, but with potassium we succeeded in superdoping the extended corannulenes, and both tetraanions $\mathbf{3}^{4-}$ and $\mathbf{4}^{4-}$ were observed and characterized. This ability of **3** and **4** to store charge when reduced with potassium is particularly significant with respect to the quest for materials that can be used, inter alia, for rechargeable organic batteries.[8]

The addition of 2 π and 4 π electrons changes the magnetic properties of **3** and **4** and, though both are extended corannulenes, their behavior on reduction is different from that observed on reduction of corannulene (**1**). The corannulenic or polycyclic character is discussed here.

Results and Discussion

The π topology of the extended corannulenes 3 and 4: The calculated potential energies (semiempirical AM1 calculations),[9] − 1.180 and − 1.558 eV for the LUMOs of **3** and **4**, respectively, are even lower than the calculated energy (− 1.028 eV) for the LUMO of **1**. Because of the high symmetry of **1** (C_{5v}), its LUMO is doubly degenerate, and thus we expected, as was later observed,[1] an easy reduction to a tetraanion. In **3** and **4**, the LUMO is not degenerate, but there is only a small energy gap between the LUMO and the NLUMO, 0.22 eV and 0.62 eV for **3** and **4**, respectively. A small energy gap between the LUMO and NLUMO could still result in the formation of highly reduced species, as has been demonstrated by Gerson and Huber.[10]

Hydrocarbon **3** exhibits aromatic character, as seen from its ^{1}H NMR spectrum (Table 1). Based on the π-topology model proposed for corannulene[4] (an annulene within an annulene), a similar π topology is suggested for **3**. According to this model, the central five-membered ring can have six electrons, thus becoming a cyclopentadienide anion with diatropic character. The other 22 π electrons can delocalize around the rim of the dibenzo[*a,g*]corannulene (**3**) giving rise, again, to diatropic character. It follows, therefore, that we have the same model for the π topology of **3**, an annulene within an annulene, as we had for **1** (Figure 2). According to this model, we should observe the same characteristics resulting from the π topology in **3** as for **1**. On the other hand, calculations (AM1)[9] predict a partial positive charge on the carbons shared by the two extra benzene rings and the corannulene moiety. This will result in a diminution of the circumference delocalization, and thus different behavior is expected for **3** relative to **1** on reduction.

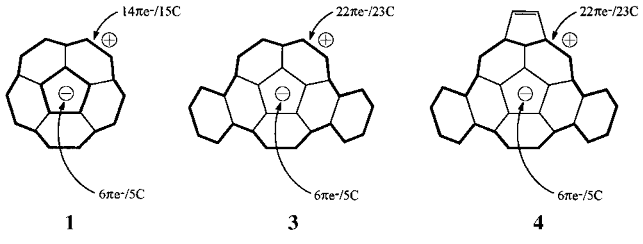


Figure 2. Annulene-within-an-annulene π topology of the neutral hydrocarbons **1**, **3**, and **4**.

If we assume that the π topology of **4** is the same as in **1** and **3**, that is, that the central hub of the five-membered ring can possess 6 π electrons, leaving the outer rim with 24 π electrons, it follows that the hydrocarbon should exhibit an antiaromatic character in its neutral form. This does not coincide with the diatropic behavior of the neutral **4** observed by ^{1}H NMR spectroscopy (Table 1). Therefore, either the two π electrons of the etheno bridge do not participate in the

Table 1. 400 MHz ^{1}H NMR and 100 MHz ^{13}C NMR parameters of **3** and **4**[a] and their anions[b] in [D$_8$]THF.

Dibenzo[*a,g*]corannulene (**3**)

	H7/H8	H6/H9	H5/H10	H4/H11	H3/H12	H2/H13	H1/H14
3	8.38	8.72	7.77	7.76	8.67	8.28	8.00
$\mathbf{3}^{2-}/2\,\mathrm{Li}^+$	2.16	4.16	5.01	5.20	4.15	2.58	1.30
$\mathbf{3}^{4-}/4\,\mathrm{K}^+$	7.05	6.17	7.36	5.60	7.28	6.07	4.72

	C7/C8	C6b/C8a	C6a/C8b	C6c/C8c	C6/C9	C5/C10	C4/C11	C3/C12	C2b/C12a	C2a/C12b	C2c/C12c	C2/C13	C1/C14	**C14a**	**C14b**
3	124.9	129.0	133.6	134.7	125.5	127.7	127.6	125.4	133.7	129.2	136.4	124.7	127.9	130.9	135.4
$\mathbf{3}^{2-}/2\,\mathrm{Li}^+$	108.9	138.9	139.7	159.3	123.4	119.8	125.8	121.3	143.1	122.2	154.3	121.0	102.2	147.5	169.5
$\Delta\delta$	−16.0	+9.9	+6.1	+24.6	−2.1	−7.9	−1.8	−4.1	+9.4	−7.0	+17.9	−3.7	−25.7	+16.6	+34.1

Dibenzo[*a,g*]cyclopenta[*kl*]corannulene (**4**)

	H8/H9	H7/H10	H6/H11	H5/H12	H4/H13	H3/H14	H1/H2
4	8.08	8.59	7.68	7.68	8.54	7.87	6.60
$\mathbf{4}^{2-}/2\,\mathrm{Li}^+$	6.70	7.89	7.00	7.00	7.81	6.15	6.04
$\mathbf{4}^{2-}/2\,\mathrm{K}^+$	6.73	7.85	7.03	7.03	7.69	6.02	6.15
$\mathbf{4}^{4-}/4\,\mathrm{K}^+$	6.57	4.84	5.01	5.01	5.60	6.10	5.95

	C8/C9	C7b/C9a	C7a/C9b	C7c/C9c	C7/C10	C6/C11	C5/C12	C4/C13	C3b/C13a	C3a/C13b	C3c/C13c	C3/C14	C2a/C14a	C2b	C2c	C1/C2
4	126.3	135.6	133.6	128.2	125.6	128.0	128.1	125.3	134.8	135.9	139.2	123.9	146.6	142.4	140.1	128.9
$\mathbf{4}^{2-}/2\,\mathrm{Li}^+$	111.2	126.1	139.4	146.4	124.2	122.6	123.4	124.2	141.8	132.0	127.0	105.8	126.2	131.8	155.3	98.5
$\Delta\delta$	−15.1	−9.5	+5.8	+18.2	−1.4	−5.4	−4.7	−1.1	+7.0	−3.9	−12.2	−18.1	−20.4	−10.6	+15.2	−30.4
$\mathbf{4}^{2-}/2\,\mathrm{K}^+$	111.6	126.2	139.4	146.5	124.3	123.4	124.2	124.4	141.3	130.3	124.6	106.7	124.8	133.8	156.6	108.1
$\Delta\delta$	−14.6	−9.4	+5.8	+18.3	−1.3	−4.6	−3.9	−0.9	+6.5	−5.6	−14.6	−17.2	−21.8	−8.6	+16.5	−20.8

[a] At room temperature. [b] At 210 K.

overall delocalization on the rim of the outer ring (Figure 2), or the π-topology model suggested for **1** and **3** does not hold in the case of **4**. In either case, we should expect a different behavior for **4** than that observed for **1** and **3** on reduction.

Reduction with lithium and the formation of dianions: Dibenzo[*a,g*]corannulene (**3**) and dibenzo[*a,g*]cyclopenta[*kl*]corannulene (**4**) were reduced with lithium metal over a period of several days, resulting in a series of three color changes in each case. The first change in the color of the solutions of both **3** and **4** to green resembles the reduction of corannulene and was accompanied by loss of the NMR spectrum. This indicates a high concentration of species with unpaired electrons in the solution, which were assigned as the radical anions $\mathbf{3}^{-\bullet}$ and $\mathbf{4}^{-\bullet}$. A second stage was observed when the solution changed color to purple. The species present at this second stage were diamagnetic in nature and exhibited well-resolved, temperature-dependent ^{1}H NMR and ^{13}C NMR spectra.

The total change in carbon chemical shifts upon charging with lithium was $\Sigma\Delta\delta = +50$ ppm in **3** and $\Sigma\Delta\delta = -178$ ppm in **4**. According to Equation (1) and taking into account the

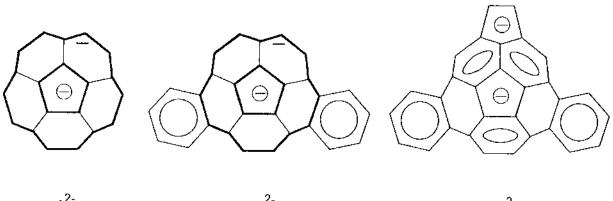
$$Kc_{(\mathrm{exp})} = \Sigma\Delta\delta/\Delta q \qquad (1)$$

two-electron reduction process, we found $Kc_{(\mathrm{exp})} = +25$ ppm and -89 ppm per unit of charge, respectively. These values are markedly different from that obtained for the corannulene dianion $\mathbf{1}^{2-}$, which has a total carbon chemical shift of +336 ppm and $Kc_{(\mathrm{exp})} = +183$ ppm/e$^-$. It seems that dianions $\mathbf{3}^{2-}$ and $\mathbf{4}^{2-}$ are missing the strong paratropic effect that operates in the dianion of corannulene and leads to very low field shifts in its carbon spectrum. This is reasonable, since the magnitude of paramagnetic ring currents is known to be inversely related to the size of the HOMO–LUMO gap,[11] and the HOMO–LUMO gaps for these dianions increase in the order $\mathbf{1}^{2-} < \mathbf{3}^{2-} < \mathbf{4}^{2-}$. This order follows from the fact that the LUMO of corannulene (**1**) is doubly degenerate, so the HOMO–LUMO gap in $\mathbf{1}^{2-}$ is only the very small ΔE imparted by Jahn–Teller distortion, whereas the HOMO–LUMO gaps in the extended dianions of lower symmetry $\mathbf{3}^{2-}$ and $\mathbf{4}^{2-}$ can be estimated from the ΔE between the non-degenerate LUMO and the NLUMO of the corresponding neutral hydrocarbons (0.22 and 0.62 eV, respectively; vide supra).[9] $Kc_{(\mathrm{exp})}$ values in the range of +25 ppm and −89 ppm/e$^-$ in $\mathbf{3}^{2-}$ and $\mathbf{4}^{2-}$ point to a characteristic feature of a polycyclic system. From the trend of the sum of the chemical shifts in the carbon NMR spectra, especially in $\mathbf{3}^{2-}$, we can infer some annulenic effect of the internal five-membered ring.

Correlations between the charge and the change in the chemical shift should be taken with a degree of caution, since Equation (1) is empirical. In our case, we are dealing with a new family of polycyclic systems that exhibit some special new properties, for example the curved structure and a special π topology. Therefore, we cannot implement the charge–shift correlation equation insouciantly. For the dibenzo[*a,g*]corannulene dianion $\mathbf{3}^{2-}$ we see that the range of ^{13}C NMR shifts is very wide, approximately 70 ppm. This exceptionally wide range indicates that two effects influence the carbon shifts. For $\mathbf{3}^{2-}$ we can divide the ^{13}C NMR shifts into two groups, one that includes the central hub carbons and a second that comprises the carbons on the outer rim of the molecule. The central hub of both dianions $\mathbf{3}^{2-}$ and $\mathbf{4}^{2-}$ is affected more by the ring current of the rim than by the charge, and as a result the lines are shifted to a relatively low field. In other words, they have an annulenic character for the central hub. The second group of carbons has shifts to a relatively high field and thus is more influenced by the charge located on the carbons, which thus have a polycyclic character. In $\mathbf{4}^{2-}$, the boundaries of the two groups are more vague, but the influence of the ring current on the carbons of the central hub is remarkable. Therefore, the equation relating the ^{13}C NMR shift displacement and the charge density can be used more safely for $\mathbf{4}^{2-}$.

In $\mathbf{4}^{2-}$**,** we find only a small negative charge density in the benzene rings, whereas the junction carbons shared by the corannulene ring and the two benzene rings (C9b, C13a, C3b, and C7a) bear a corresponding amount of positive charge. It therefore appears that the majority of the extra charge density in $\mathbf{4}^{2-}$ is concentrated in the central ethenocorannulene unit, and the polarizable π electrons in each of the fused benzene rings respond by shifting slightly away from the ring junction. High charge density was found on the carbons of the peripheral corannulene ring. The external five-membered ring in compound $\mathbf{4}^{2-}$ exerts a strong charge-withdrawing effect.

By comparing the difference of the carbon chemical shifts relative to corannulene dianion $\mathbf{1}^{2-}$, we can draw a number of conclusions. Firstly, changes of the peripheral π system of corannulene can affect the electronic properties of this compound dramatically, and secondly, it can be shown that the addition of the two benzannelated rings (i.e., **3**) exerts a relatively small distortion on the corannulene π system while the addition of a five-membered ring (i.e., **4**) can change the annulenic behavior of **1** significantly. Although no single structural representation can completely reflect all of the properties of either of these two dianions, $\mathbf{3}^{2-}$ can probably be best thought of as a perturbed relative of the corannulene dianion $\mathbf{1}^{2-}$, which has an aromatic 6 π-electron hub inside an antiaromatic 16 π-electron annulene rim (Figure 3); the two fused benzo rings on **3** partially quench the paramagnetic ring current of the antiaromatic 16 π-electron annulene rim. Dianion $\mathbf{4}^{2-}$**,** on the other hand, is probably better represented as a species with less prominent contributions of the antiaromatic cycles and relatively isolated fused benzo rings.



$\mathbf{1}^{2-}$ $\mathbf{3}^{2-}$ $\mathbf{4}^{2-}$

Figure 3. Structural representations that reflect the highly paratropic nature of the corannulene dianion ($\mathbf{1}^{2-}$), the more weakly paratropic nature of the dibenzo[*a,g*]corannulene ($\mathbf{3}^{2-}$), and the diatropic nature of the dibenzo[*a,g*]cyclopenta[*kl*]corannulene ($\mathbf{4}^{2-}$).

Another point which should be considered is that the carbon framework of compound **4** includes a [5,5]fulvalene unit. One of the rings of the fulvalene is in the hub of the corannulene system, and the other one is on the periphery. This fulvalene unit, which is normally stabilized by charge alternation, becomes asymmetrically charged in the dianion $\mathbf{4}^{2-}$, where the external ring is highly negatively charged. It is not unreasonable that the tendency to stabilize a dipolar fulvalene leads to a significant distortion of the corannulene π system.

The centers of gravity in the ^{1}H NMR spectra of $\mathbf{3}^{2-}$/2Li^{+} and $\mathbf{4}^{2-}$/2Li^{+} show paratropic shifts of 4.72 and 0.92 ppm, respectively. Despite the structural similarity of these two systems, we find them quite different in their proton chemical shifts. The explanation for the different behavior of the charged species can be attributed to two different effects: the charge on the carbons and the ring current effect. Similar to the 14 π electrons of the corannulene rim in its neutral form, the extended peripheral structure of both **3** and **4** consist of 22 and 24 π electrons, respectively. In its neutral form **4** has aromatic characteristics under the influence of a magnetic field. Thus, the two extra π electrons of the ethene bridge on carbons C1 and C2 do not participate in the overall conjugation. On reduction to dianions, $\mathbf{3}^{2-}$ becomes $4n$ antiaromatic and $\mathbf{4}^{2-}$ can become a $4n+2$ aromatic system if the two π electrons of the bridge participate in the overall delocalization of the π electrons of the rim (Figure 3). Aromatic systems are expected to sustain a diatropic ring current that causes a considerable downfield shift of nuclei located in the molecular plane outside the ring. An upfield, paratropic, shift is expected in antiaromatic systems. Combining the ring current effect with the effect due to the extra charge, we find the ^{1}H NMR lines of $\mathbf{3}^{2-}$ to be shifted to a higher field than those of $\mathbf{4}^{2-}$. It therefore follows that an opposite effect in the case of tetraanionic species should be expected, and such is indeed the case when both systems are doped with 4 π electrons (vide infra).

Both systems $\mathbf{3}^{2-}$ and $\mathbf{4}^{2-}$ differ significantly from $\mathbf{1}^{2-}$ in their ^{1}H and ^{13}C NMR spectra, as was described earlier. In $\mathbf{1}^{2-}$, a very strong paratropic shift of 13.5 ppm was observed, compared with 4.72 and 0.92 ppm for $\mathbf{3}^{2-}$ and $\mathbf{4}^{2-}$, respectively, emphasizing the difference between an annulene and a benzannelated annulene. Here again we see that the magnitude of the paratropic ring-current effect diminishes as the HOMO–LUMO gap increases.

The annulene-within-an-annulene model for the charge delocalization pattern in **1** can not be fully applied for the description of the electronic properties of **3** and **4** and their metal salts. Owing to distortion of the corannulene peripheral π system, **3** and **4** behave rather like large conjugated polycyclic systems with some annulenic features, which are more pronounced in **3** than in **4** (Figure 3).

The ^{7}Li NMR spectra of dianions $\mathbf{3}^{2-}$ and $\mathbf{4}^{2-}$ each exhibit one single line ($\delta = -0.5$ and -2.8, respectively). No significant changes in the spectral features were observed between 170 and 300 K. One single line independent of temperature is consistent with a monomer species at this stage of charging. However, it should be noted that the formation of a dimer was observed only in the last stage of the reduction of **1**, that is, the reduction to a tetraanion. Both anionic systems $\mathbf{3}^{2-}$ and $\mathbf{4}^{2-}$ maintain solvent-separated ion-pair (SSIP) interactions with the lithium cations, and the difference in lithium chemical shifts can be assigned to an isotropic effect. Location of the lithium cations above or below the center of the anionic system, thus forming an ion triplet, is expected to lead to a chemical shift in the opposite direction to that of the protons on the rim. The total effect is still small because of the weak interaction operating between the anion and the cation.

Further contact with the lithium metal led to a slow disappearance of the NMR spectrum, suggesting formation of another paramagnetic stage, presumably radical trianions $\mathbf{3}^{3-\bullet}$ and $\mathbf{4}^{3-\bullet}$. At this stage the reduction of **3** and **4** ceased, and no further reduction was observed.

Increasing the concentration might promote a dimerization process, which in turn would promote the formation of a higher reduction stage. However, no further reduction stage, to a tetraanion, was observed for several months in several samples with even higher concentrations. The relatively low reduction potential of lithium and the inability of the systems to form dimers, which could stabilize the charged species, are the two main reasons why a tetraanion was not formed.

Reduction with potassium; supercharged extended corannulenes: The use of a different alkali metal, that is, potassium, for the reduction offered some surprising results. At first, we anticipated that employing potassium metal for the reduction of **3** and **4** would afford the same results observed for **1**, that is, that the highest reduction stage for **3** and **4** would be the trianion radical stage. However, we encountered totally different behavior from that observed for **1**.

The first reduction stage with potassium yielded a green solution, as in the reduction with Li. This stage was assigned to the formation of radical anions $\mathbf{3}^{3-\bullet}$ and $\mathbf{4}^{3-\bullet}$, for which no NMR spectrum can be detected. The second stage afforded a purple solution and well-resolved temperature-dependent ^{1}H and ^{13}C NMR spectra. The ^{1}H and ^{13}C chemical shifts for $\mathbf{3}^{2-}/2\,\mathrm{K}^+$ are identical to those observed for the reduction product with lithium ($\mathbf{3}^{2-}/2\,\mathrm{Li}^+$). However, there are some differences in the ^{1}H and ^{13}C spectra of the reduction product of **4** with potassium ($\mathbf{4}^{2-}/2\,\mathrm{K}^+$) as compared with $\mathbf{4}^{2-}/2\,\mathrm{Li}^+$. We found the total changes in the ^{13}C chemical shifts ($\Sigma\Delta\delta$) to be $+50$ and -160 ppm for $\mathbf{3}^{2-}/2\,\mathrm{K}^+$ and $\mathbf{4}^{2-}/2\,\mathrm{K}^+$, respectively. Small changes in the ^{1}H chemical shifts were also observed for $\mathbf{4}^{2-}/2\,\mathrm{K}^+$ relative to the ^{1}H NMR of $\mathbf{4}^{2-}/2\,\mathrm{Li}^+$. For the potassium salt of **4** ($\mathbf{4}^{2-}/2\,\mathrm{K}^+$) we observed less negative charge on the external five-membered ring, and now more charge is accommodated on the adjacent carbons (C13b, C13c, C14a, C2a, C3a, C3c). The rest of the molecule displayed a similar charge delocalization pattern to that observed for $\mathbf{4}^{2-}/2\,\mathrm{Li}^+$. We attribute this difference to the tendency of the smaller lithium cations, which have a higher charge density when compared to potassium, to lead to some charge localization on the anionic system.

The formation of new paramagnetic species, the radical trianions $\mathbf{3}^{3-\bullet}$ and $\mathbf{4}^{3-\bullet}$, could be followed as the spectra of the diamagnetic species gradually disappeared. After a while, a fourth stage was observed with a change in the color of the solution to brown. This fourth stage exhibited entirely different ^{1}H NMR spectra from those observed for the first diamagnetic stage $\mathbf{3}^{2-}$ and $\mathbf{4}^{2-}$. The ^{1}H NMR lines for both compounds were rather broad even at low temperatures ($T \leq 200$ K). A chemical reaction product (for example protonation) due to the reduction was excluded when a quench reaction with oxygen yielded only the pure starting materials **3** and **4**. Once the possibility of a chemical reaction had been ruled out, we assumed that these new diamagnetic species were the tetraanions of **3** and **4** ($\mathbf{3}^{4-}$and $\mathbf{4}^{4-}$, respectively). To confirm our assumption we used D_2O to quench the reaction product. Mass spectroscopy of the quenched products shows that the main products are the tetradeuterio derivatives of dibenzo[*a,g*]corannulene ($m/e = 358$) and of dibenzo[*a,g*]cyclopenta[*kl*]corannulene ($m/e = 382$). Although the ^{13}C NMR spectra of these species could not be obtained over a wide temperature range, the quench with D_2O and the resolved ^{1}H NMR spectra indicate clearly that tetraanionic species are formed. Tetraanions $\mathbf{3}^{4-}$ and $\mathbf{4}^{4-}$, to the best of our knowledge, are the first known conjugated benzenoid compounds of such size and shape that bear four charges with potassium as a countercation.

Despite the additional charge, the center of gravity of the chemical shifts in the ^{1}H NMR spectrum of $\mathbf{3}^{4-}$ is shifted to a lower field ($\delta_{\text{center of gravity}} = 6.32$) than that of $\mathbf{3}^{2-}$ ($\delta_{\text{center of gravity}} = 3.51$), indicating the diatropic character of this new species. In the case of tetraanion $\mathbf{4}^{4-}$ we see the effect of the extra negative charge and the ring current effect in this novel $4n$ antiaromatic system influence the chemical shifts in the same direction. Therefore, the center of gravity of the ^{1}H chemical shifts in the tetraanion $\mathbf{4}^{-4}$ appears at a higher field ($\delta_{\text{center of gravity}} = 5.58$) than that of $\mathbf{4}^{2-}$ ($\delta_{\text{center of gravity}} = 6.93$), as can be expected for a $4n\,\pi$ system (antiaromatic).

There is an obvious difference between the behavior of corannulene (**1**) and the extended corannulenes **3** and **4** under the reduction reaction. Potassium is known to be a better reducing agent in organic solvents. Because of the large cationic radius of K^+ compared to Li^+, it also has a thinner solvation shell. It therefore follows that potassium forms tighter ion pairs with the anion in the solution. In general, these properties give potassium a better chance than Li to form multicharged systems such as radical trianions.[10] In the case of corannulene (**1**), we observed the opposite behavior; lithium was the reducing agent that formed the tetraanion $\mathbf{1}^{4-}$ in significant amounts while potassium did not show reduction products beyond the radical trianion. The lithium salt $\mathbf{1}^{4-}/4\,\mathrm{Li}^+$ is formed because of the dimerization to **2**, which stabilizes the countercations of the tetraanion. The π systems of **3** and **4** are probably large enough to accommodate up to four negative charges and the countercations in their proximity with minimum Coulomb repulsion, allowing further reduction yielding supercharged extended corannulenes with the stronger reducing metal, that is, potassium.

Although **3** and **4** are extended corannulenes, it seems that once reduced with lithium they do not tend to form dimers, unlike **1**, and this accounts for their failure to form a tetraanion with lithium. One reason for this behavior is the different charge delocalization patterns of these molecules. While for **1** we observed a homogeneous charge delocalization in an annulene-within-an-annulene pattern, in the case of **3** and **4** the ^{13}C NMR spectra of the dianions show that the conjugated extra benzene rings and the five-membered ring break this pattern (Figure 3). Complete charge dispersion in the tetraanions of **3** and **4**, where the charge density on the entire carbon skeleton is smaller than the charge density on the corannulene tetraanion $\mathbf{1}^{4-}$, would lead to less tightly bound Li cations. Thus in this case the Li cations do not serve as the glue that the two anionic decks need for dimer formation. Therefore, the dimerization of **3** or **4**, each with itself, does not occur when they are reduced with Li, and no tetraanions are formed. We see that the formation of a dimer in these systems is essential for the formation of a tetraanion when Li is the reducing agent. These results are in line with the reduction mechanism proposed for **1**,[5] where the formation of the sandwich-type structure occurs only at the last stage of the reaction, that is, the reduction to the tetraanion, and the formation of the tetraanion is consequently dependent on the formation of a dimer with lithium cations acting as the glue.

Conclusions

In conclusion, it can be seen that the benzannelation of corannulenes modifies the π topology, and the charge delocalization pattern in the coresponding anions is also changed. It can then be calculated that **3** and **4** have the characteristics of large polycyclic systems with some annulenic character rather than the more pronounced annulene character of **1**. The ring-current effect of the central five-membered ring in **4** is smaller, and this may be due to a greater distortion of the original π topology of corannulene caused by the additional conjugated five-membered ring.

In general both systems, **3** and **4**, behave similarly upon reduction, although their different π topologies give opposite characteristics in a magnetic field (i.e., NMR).

The charge density per carbon atom in both systems is lower than in corannulene, and that causes **3** and **4** to remain monomers when reduced with lithium. As monomers, **3** and **4** can only be triply charged, and a forth reduction stage that could be stabilized by dimerization is not observed with lithium.

The extended corannulenes **3** and **4** undergo a fourth reduction stage when reduced with potassium. In the quest for new organic materials for rechargeable organic batteries, the ability of **3** and **4** to store high amounts of charge with minimum Coulomb repulsion is a very attractive quality.

Experimental Section

All NMR analyses were performed on Bruker AMX400 and Bruker DRX400 pulsed FT spectrometers operating at 400.13, 100.62, and 155.51 MHz for ^{1}H, ^{13}C, and ^{7}Li NMR, respectively. Full structure assignment was obtained by applying 2D–NMR spectroscopies such as COSY, NOESY, CH correlation and LRCH correlation.

Materials: Potassium and lithium (Aldrich) were kept in paraffin oil and were rinsed shortly before use with petroleum ether (b.p. 40–60 °C). [D$_8$]THF (Aldrich) was dried over potassium–sodium alloy under vacuum.

The reduction process: Lithium wire or potassium mirror was introduced to the upper part of an extended NMR tube containing the compounds dissolved in [D$_8$]THF. The sample was degassed and sealed under vacuum. The solution was brought into contact with the metal solution by turning the tube upside down.

Quenching of the anions: All anions were quenched with oxygen or D_2O. The oxygen quenching experiments were carried out by bubbling the gas into the NMR sample tube under anhydrous conditions. Oxygen gas was slowly bubbled through a syringe into the cold anion solution, the dark color disappeared, and the ^{1}H NMR spectrum was recorded. Quench experiments with D_2O were followed by MS analysis.

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