

Corannulene Reduction: Spectroscopic Detection of All Anionic Oxidation States

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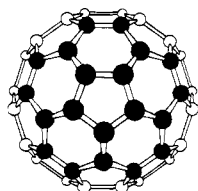
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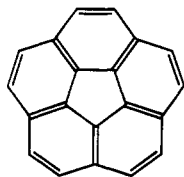
Abstract: The reduction of corannulene (**1**) has been followed by parallel detection of optical absorption, electron paramagnetic resonance (EPR), and nuclear magnetic resonance (NMR) spectroscopies. The major findings are the existence of a diamagnetic dianion that can be observed in NMR and negligible counterion influences in the mono- and dianion. The diamagnetic state of the dianion is also supported by vanishing EPR intensity and semiempirical calculations and exhibits one indistinguishable proton NMR resonance at -5.6 ppm for potassium and lithium as counterions, respectively. The NMR signal is strongly temperature dependent and can only be obtained at low temperature ($T < 230$ K) where the line width decreases with temperature. Further reduction to the trianion and tetraanion succeeds with Li as the reducing metal, but not with K even at ambient temperatures. The EPR spectra of the trianion show a pronounced temperature dependence with at least two Li cations being strongly coupled.

Introduction

The convex surface of C_{60} owes its curvature to the pyramidalization of trigonal atoms that are each located at the confluence of one 5-membered ring and two 6-membered rings. The presence of five such pyramidalized carbon atoms around the center of corannulene (**1**) imparts a similar curvature to this fullerene subunit, just as predicted by Barth and Lawton, who first synthesized and named corannulene in 1966.¹ Shorter new



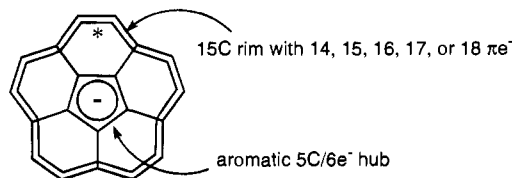
C_{60}



corannulene (**1**)

synthetic routes to **1** have recently opened the door to extensive investigations on the chemical and spectroscopic properties of this prototypical bowl-shaped hydrocarbon,² and parallels with the properties of fullerenes have already begun to emerge. For example, C_{60} has a triply-degenerate, low-lying LUMO (lowest unoccupied molecular orbital) that can accept up to six extra electrons,³ and corannulene has a doubly-degenerate, low-lying LUMO that can accept up to four extra electrons.⁴ We first published the 1H and ^{13}C NMR spectral properties of the

corannulene tetraanion (1^{4-}) in 1992⁴ and subsequently reported on the unexpected aggregation of this species to form a high-order molecular sandwich with four lithium atoms held tightly between the two hydrocarbon tetraanions.⁵ The corannulene tetraanion (1^{4-}) can best be thought of as an aromatic 5C/6e hub suspended within an aromatic 15C/18e rim, i.e., concentric anions or an "annulene within an annulene".^{4,6} Neutral corannulene was originally visualized by Barth and Lawton as an aromatic 5C/6e core suspended within an aromatic 15C/14e rim, likewise an "annulene within an annulene".^{1,6} The work described in this paper examines the reduction states of corannulene that lie between the neutral hydrocarbon and the tetraanion, i.e., the radical monoanion ($1^{\cdot-}$), the dianion (1^{2-}), and the trianion (1^{3-}), all of which can be thought of as species composed of aromatic 5C/6e hubs and 15C rims around which varying numbers of π electrons circulate. Of particular interest



is the previously unknown corannulene dianion (1^{2-}) and the question of whether it is paramagnetic or diamagnetic. A 5-fold symmetric species should have a triplet ground state, but Jahn–Teller distortion is expected to split the degeneracy of the half-filled energy level and lead to a ground state singlet with a low-

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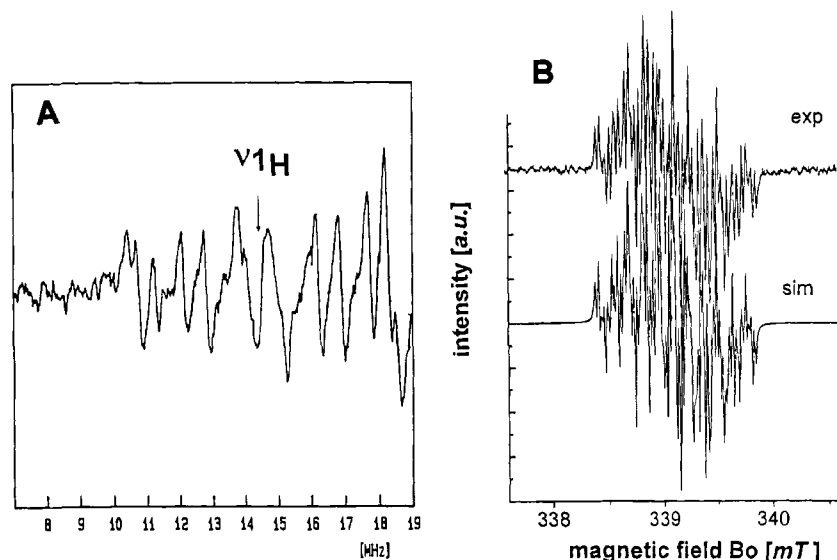


Figure 1. ENDOR (A) and EPR (B) spectra of $2^{\bullet-}$ together with the computer-simulated EPR spectrum.

Table 1. Optical Absorption Data (nm) for **1** and **2** in THF

	1	2
monoanion	443, 648, 805, 904	442, 665, 805, 903
dianion	387, 503	377, 515
trianion	428, 575, 710	428, 578, 717
tetraanion	740	

lying triplet state. The stage of reduction at which dimers are formed is also of interest.

Herein we report on parallel EPR/ENDOR, optical absorption, and NMR spectroscopic measurements to define the nature of the anions with potassium and lithium as counterions. All five reduction stages from 1^0 to 1^{4-} have now been characterized.

Experimental Section

The corannulenes **1** and **2** have been synthesized according to established procedures.^{2a,b,7} The reduction was performed in special glass/quartz sample tubes under high vacuum in THF- d_8 , and the sample was dried over Na/K alloy with Li wire pressed into the reduction chamber or K sublimed as mirror on the surface of the reduction chamber.⁸

Optical absorption measurements were done with a Perkin Elmer Lambda 9, and EPR/ENDOR spectra have been recorded on a Bruker ESP 300 at X-band frequency (9.43 GHz) with 100 (EPR cavity) and 12.5 (ENDOR cavity) kHz field modulation, respectively. For g -value determination DPPH ($g = 2.0037$) as standard was used in addition to a digital frequency counter Modell 3120 (XL microwave) and an ER035M NMR gaussmeter (Bruker). The ^1H , ^{13}C , and ^7Li NMR spectra were determined in THF- d_8 (99.5%; Deutero GmbH, D-56729 Herresbach) on Bruker AMX-500 (Mainz; ^1H (500 MHz), ^{13}C (125 MHz), and ^7Li (194.3 MHz)) and AMX-400 (Jerusalem) spectrometers.

Results

Controlled reduction of corannulene with alkali metals (Li and K) in THF- d_8 solution under high vacuum⁸ results in a green solution with optical absorption bands at $\lambda_{\text{max}} = 443, 648, 805,$ and 904 nm (Table 1). The EPR spectrum shows an 11-line hyperfine pattern ($a_{\text{H}} = 0.157$ mT) for the ten equivalent protons (see also ref 9). Differences between K and Li as counterions

Table 2. EPR/ENDOR Data for $1^{\bullet-}$, 1^{3-} , and $2^{\bullet-}$ in THF

	$1^{\bullet-}$	$2^{\bullet-}$	1^{3-}
g -value	2.0027	2.0027	2.0025
a_{H} (mT)	0.157	0.289(1), 0.269(2), 0.231(1), 0.171(1), 0.122(1), 0.047(1), 0.030(2)	0.162
a_{Li}			0.075–0.080 (2)

are negligibly small, and no counterion coupling was resolved in either case ($g = 2.0027$, $a_{\text{H}} = 0.157$ mT (K and Li)).

Radical anion $1^{\bullet-}$ did not undergo microwave power saturation even at 200 K under conditions necessary for highly resolved ENDOR studies.¹⁰ We attributed this behavior to the high symmetry of $1^{\bullet-}$ and therefore reduced the monoalkylated derivative *tert*-butylcorannulene (**2**).⁷ The substituent in $2^{\bullet-}$ does not change the chromophoric properties significantly (Table 1), and the ENDOR measurements performed at 190–200 K (Figure 1A) indeed allowed resolution of at least eight different proton hyperfine couplings (hfc's). The experimental EPR spectrum was reproduced well by computer simulation (Figure 1B) using the multiplicity of measured proton hfc's given in Table 2.

Upon further reduction the samples turn red, but continue to exhibit the same EPR spectra. Finally the EPR intensity decreases, and the samples become diamagnetic with a parallel increase of new absorption bands in the electronic spectra ($\lambda_{\text{max}} = 387, 503$ nm) (vide infra). These new diamagnetic species, i.e., dianions 1^{2-} , show reversible temperature dependent broad ^1H NMR spectra with just one signal at -5.6 ppm (Figure 2A, Table 3), which disappears completely at higher temperatures ($T > 230$ K). Changing the alkali metal from potassium to lithium has no effect on the ^1H NMR spectrum (Figure 2B). The extreme high field shift of the protons is typical for molecules with paratropic ring current effects.^{11,12} Thus diamagnetic 1^{2-} may be viewed as consisting of an aromatic (diatropic) cyclopentadiene anion in the center and an antiaromatic (paratropic) 16π perimeter, where it is the shielding effect of the outer ring current that shifts the signal to -5.6 ppm. The ^1H NMR spectra are consistent with a description of 1^{2-} as an

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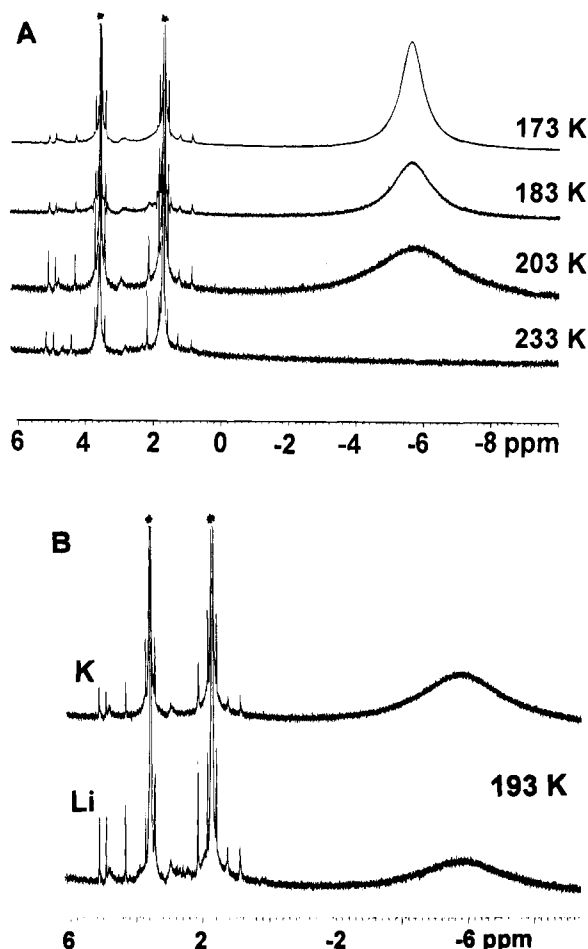


Figure 2. ¹H NMR spectra for 1²⁻/K²⁺ in THF (*) at 173–233 K (A) and comparison of 1²⁻/K²⁺ with 1²⁻/Li²⁺ at 183 K (B).

Table 3. NMR Spectroscopic Results (500 MHz) for 1²⁻ and 1⁴⁻ in THF-*d*₈

(A)	1 ²⁻	¹ H (183 K): -5.6 ppm (K ⁺ and Li ⁺ are indistinguishable)
(B)	1 ²⁻	¹³ C (305 K): 204, 154, 120 ppm (K ⁺); 203, 154, 120 ppm (Li ⁺)
(C)	1 ²⁻	⁷ Li: 3.3 (220 K); 3.7 ppm (170 K)
(D)	1 ⁴⁻	¹ H (295 K): 6.92 ppm
(E)	1 ⁴⁻	¹³ C: 112 (quaternary), 95 (quaternary), 87 (tertiary) ppm
(F)	1 ⁴⁻	⁷ Li (170 K): -4.2, -11.51 ppm

“annulene within an annulene”, analogous to that suggested by Ayalon et al.^{4,5} for 1⁴⁻ but with the outer cycle now being antiaromatic.

The reversible temperature dependent changes in the ¹H NMR spectrum of 1²⁻ are striking and deserve an explanation. We ascribe this phenomenon to effects of mixing low-lying triplet states into the electronic structure of 1²⁻ as the temperature rises. Quantum chemical calculations at the semiempirical level of theory (AM1)¹³ predict a singlet ground state for 1²⁻ but put the triplet excited state only 0.24 eV higher in energy, which is close enough to be thermally accessible. Temperature variations also influence the degree of ion pairing, which in turn will affect the singlet–triplet energy gap. Such temperature dependent ¹H NMR behavior has been reported previously, both for anions¹⁴ and for neutral “biradicaloid” hydrocarbons,¹⁵ and the effect has generally been traced to a low-lying triplet state. Consider-

ing the field effect for the Zeemann levels of the triplet states, the high-field approximation in the NMR ($B_0 = 11.7$ mT) should even lead to enhanced triplet mixing compared to the low-field conditions found in EPR (B_0 ca. 0.34 mT).

The ¹³C NMR of the dianion shows single peaks at 204, 154, and 120 ppm, together with very weak features of protonated side products or small paramagnetic contributions. The extremely low field signal of quaternary carbon at 204 ppm presumably corresponds to the cyclopentadiene carbon atoms in the center of 1²⁻. This unusual chemical shift can be explained easily by the strong deshielding effect of the outer ring current within the model mentioned above.

The dianion does not seem to share the same exceptional behavior of the tetraanion, which undergoes dimerization, but rather exists as a separate monomer with two Li cations. This view finds support not only from the above ¹H and ¹³C NMR spectra but also from the temperature dependent ⁷Li NMR measurements, where the absence of splitting upon decreasing the temperature indicates a common Li binding site.^{16,17} The ⁷Li NMR exhibits just one broad absorption around 3.7–3.3 ppm ($T = 173$ – 220 K), relatively close to the ⁷Li frequency that is typical for loose ion pair structures.^{11,12,16,17} A pronounced sharpening of the line width upon decreasing the temperature parallels the effect described earlier for the ¹H NMR spectra and presumably reflects the same singlet/triplet mixing. We hesitate to draw any conclusions from the position of the ⁷Li NMR signal, since the shift depends not only on the dia- and paratropic ring currents but also on the solvent, concentration, and temperature.^{11,12,16–18}

Trianion formation was found only for the Li samples. While the majority of the compound reduced with excess potassium remains in the dianionic state, some weak paramagnetic side products are formed, which are due to partially protonated species as judged from their EPR spectra. The trianion with Li exhibits new optical absorption bands at 428, 575, and 710 nm, together with a highly resolved EPR spectrum centered at $g = 2.0025$, where additional ⁷Li couplings are evidenced ($a_{\text{H}} = 1.62$ mT, $a_{\text{Li}}(I=3/2) = 0.04$ – 0.10 mT). Varying the temperature between 200 and 290 K causes reversible changes in the appearance of the EPR spectrum, presumably as a result of tightening and loosening the association of the ⁷Li ions.¹⁸ The computer simulation of the experimental EPR spectrum gives good agreement when two equivalent lithium counterions ($T = 200$ K; $a_{\text{Li}} = 0.075$ – 0.080 mT) are taken into account (Figure 3).

It is of special importance to note that no change of the characteristic hyperfine pattern could be observed in the EPR spectra of the trianion at 200 K over the entire reduction stage from the di- to the tetraanion, which is indicative of no change in the number of coupled counterions. These findings, together with the reversible temperature dependent behavior with no decrease of EPR signal intensity upon cooling, unambiguously excludes a dimerization process for the trianion.

Complete tetraanion formation is difficult to achieve and often proceeds after long contact times with Li (days to weeks). In some cases, on the other hand, the NMR spectroscopic control of reduction even allowed parallel detection of decreasing dianion signal accompanied by appearance of the new signals

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Scheme 1. Suggested Reduction Pathway of 1

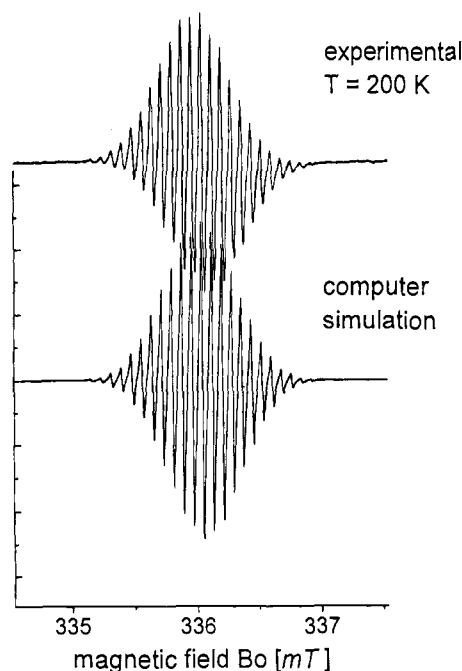
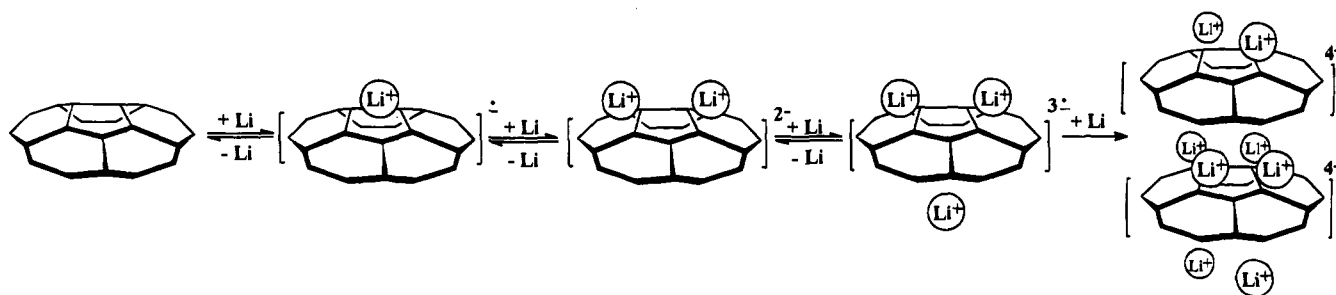


Figure 3. Experimental EPR spectrum of $1^{3-}/2Li^+$ in THF at $T = 200$ K together with the computer simulated EPR spectrum with two equivalent lithium hfc's ($a_{Li}(I=3/2) = 0.08$ mT).

for the tetraanion, both in 1H and 7Li NMR. These observations led us to suggest the reaction path shown in Scheme 1 for the reduction of corannulene. In the course of corannulene reduction, monomeric states $1^{•-} - 1^{•3-}$ are all observed. Exhaustive reduction gives the tetraanion, which dimerizes very rapidly and, due to its high stability, does not seem to exchange with the trianion radical. Consequently, the formation of tetraanion can be measured by NMR without line broadening effects from the presence of trianion radical.

The NMR spectra of 1^{4-} are identical with those reported earlier without strong temperature variation (1H absorptions at 6.92 ppm; ^{13}C absorptions at 87.35, 95.15, and 112.33 ppm).

The ^{13}C signal at 87.35 ppm is most pronounced and, according to spin-echo measurements, belongs to the tertiary carbons as suggested earlier.

Conclusion

The hitherto unknown dianion of corannulene has been prepared and shown to exist as a stable diamagnetic species. A large paratropic ring current associated with the 16-electron conjugated circuit around the perimeter of this dianion strongly shields the attached protons (-5.6 ppm; 1H NMR) and strongly deshields the interior carbon atoms (204 ppm; ^{13}C NMR). The trianion radical of corannulene has also been prepared and studied spectroscopically for the first time. A pronounced counterion effect is observed. Thus, reduction to the trianion and tetraanion can be achieved with lithium, whereas reduction with the larger potassium stops at the dianion stage. Neither the diamagnetic dianion nor the trianion radical shows any indication of aggregating to form dimers analogous to those previously seen for corannulene tetraanions with lithium counterions.

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Supplementary Material Available: Three figures: Figure 4, Optical absorption spectra of 1 for the mono- to trianion, Figure 5, 7Li NMR of 1^{2-} (Li^+/THF), Figure 6, Temperature-dependent EPR spectra of $1^{3-}/Li^+$ in THF (300–250 K) (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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