# Concerning the Structure of the Corannulene Tetraanion.

Peter W. Rabideau,* Zbigniew Marcinow, Renata Sygula and Andrzej Sygula

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803

Abstract: The question of an anion within an anion structure for corannulene tetraanion is examined by ab initio and semi-empirical calculations, as well as by the behavior of corannulene anionic intermediates in anhydrous ammonia. Calculations do not lend much support to a central cyclopentadienyl anion in the tetraanion, and a tetraanion is either not formed or does not resist protonation in liquid ammonia.

The discovery that buckminsterfullerene, C_{60}, is a stable molecule due to geodesic and electronic properties inherent in the truncated icosahedral cage structure[1] has generated renewed interest in curved-shaped hydrocarbons that resemble a portion of the buckminsterfullerene surface. For example, the carbon framework
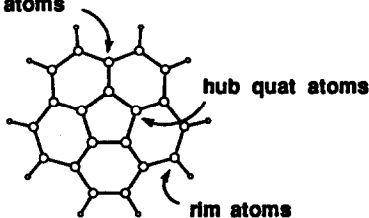

1

of corannulene (**1**) represents the polar cap of buckminsterfullerene. Although the synthesis of **1** was first achieved by Barth and Lawton in 1966,[2] this interesting, bowl-shaped molecule remained relatively unaccessible, due to the difficulty of the original method, until the recent work of Scott and coworkers.[3,4]

Corannulene is easily reduced electrochemically and by alkali metals.[5] Electron addition initially produces a radical anion (green solution in THF) that subsequently undergoes further reduction to a red species originally identified only as a decay product of the dianion.[5] More recently, it was concluded from NMR[6] that the final
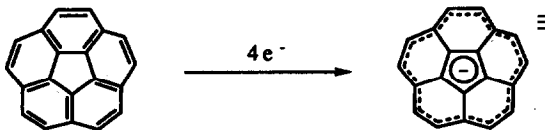
reduction product of **1** by lithium in THF is the tetraanion. These authors made the interesting suggestion that this tetraanion may be an "anion within an anion." That is, the tetraanion may be viewed as a cyclopentadienyl anion inner core, with the remaining 3 electrons at the periphery of the molecule producing an 18-π (i.e., 4n+2) electrons) trianion. Herein we explore the viability of this fascinating structure by both theory and experiment.

Molecular orbital calculations carried out at both semiempirical AM1[7] and ab initio[8] levels suggest that the tetraanion structure may be more complicated than the highly symmetrical "anion in a trianion" model. First, the optimized structures calculated at AM1 and ab initio 3-21G[9] levels are nonplanar. The distance between the planes defined by the hub atoms and the rim atoms is predicted by 3-21G calculations to be 0.37Å for the isolated tetraanion, albeit somewhat flatter than predicted for neutral 1 (0.88Å in excellent agreement with the experimental value of 0.89Å). Moreover, the C_{5v} constrained geometry is not the energy minimum at the Hartree-Fock level of approximation since it exhibits imaginary frequencies (3-21G; two-fold degenerate vibration, 793i). The true minimum has C_s symmetry with a total energy lower than the C_{5v} tetraanion by 1.7 (3-21//3-21G) or 3.0 kcal/mol (6-31G*//3-21G). On the other hand, inclusion of electron correlation at the MP2/3-21G level[10] strongly favors the latter structure by 16.7 kcal/mol. However, the charge distribution is essentially the same for both geometries, and we will use the C_{5v} structure for comparisons below.

Excess electron densities from the ab initio calculations together with values calculated from NMR data[6] using the value of 174.87 ppm/e[11] are presented in Table 1. The theoretical results, which are for the isolated tetraanion, show the rim atoms to bear 3.430e excess (-0.3430 each), as compared to 0.468 electrons shared by the five hub quat atoms (-0.0936 each), and 0.032 electrons spread over the rim quat atoms (-0.0064 each).

Table 1. Excess Electron Densities in Corannulene Tetraanion.

| Positions	Ab Initio Calculations[a]	^{13}C NMR[b]
rim CH	3.430	2.28
rim quat	0.032	1.0
hub	0.468	0.64

a. Difference between C_{5v} neutral 1 and C_{5v} isolated tetraanion; Mulliken population analysis with the 3-21G basis set.[12] b. Tetralithio derivative; calculated from data contained in reference 6.

The anion in a trianion structure would, of course, require 3.0e excess in the rim (rim + rim quat) and 1.0e excess in the cyclopentadienyl moiety. Hence, at least in the gas phase, the inner ring is not expected to gain sufficient negative charge in the tetraanion formation so as to resemble a cyclopentadienyl anion.

A similar distribution of negative charge was obtained at the semiempirical level. AM1 predicts the central ring to gain ca. 0.5 electrons while the ten C(H) groups gain ca. 3.5 electrons and the charge of the quaternary rim carbons remains almost unchanged. This close agreement between semiempirical and ab initio results suggests that the charge distribution is not an artifact of the method used. Calculation of electron densities from ^{13}C chemical shifts indicates a slight shift of negative charge toward the central position; however the excess charge (0.64e) is still significantly less than that expected for a cyclopentadienyl center. Given that the NMR electron densities come from a solvated species with four counterions, while the theoretical results are for a gas phase anion, the charge distribution differences between the rim and hub atoms are rather similar.

One characteristic of especially stable polyanions is their stability (lack of reactivity) in liquid ammonia. For example, cyclooctatetraene, aceheptylene and perylene react with alkali metals in ammonia to produce

dianions that resist protonation and can be dialkylated.[14] Less stable anions are too basic to exist in this relatively acidic medium; for example, dianions of anthracene, azulene, naphthalene, phenanthrene, and
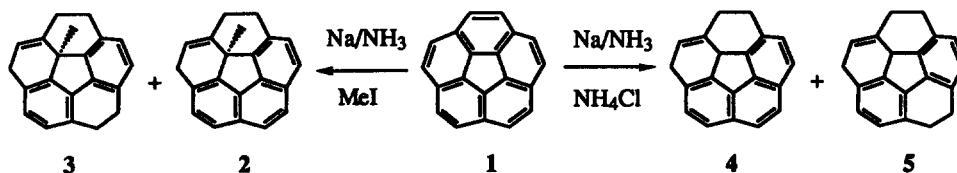
pyrene.[14] Since 1-tetraanion has a carbon to charge ratio that is comparable to (or exceeds) these stable polyanionic species, its behavior in ammonia might lend insight into any special structural characteristics. The addition of excess sodium to **1** in anhydrous ammonia[15] followed by inverse quenching into NH$_4$Cl solution produced tetrahydrocorannulene **4**[16a] (mp 185-187 °C; 63% by GC), and hexahydrocorannulene **5**[16b] (mp 123-125 °C; 37%). With THF as cosolvent, **5** becomes the major product (90%). Quenching of the ammonia/THF solution into MeI/THF produced the monomethyl derivatives **2**[16c] and **3**,[16c] with **3** predominating (80%). The fact that four or six hydrogens can be easily incorporated, while only one methyl can be introduced, argues against the presence of a stable tetraanion. In fact, it cannot be determined whether or not a tetraanion is formed at all under these conditions. The monoalkylation results suggest that monoanions **6** and **7** are present at the
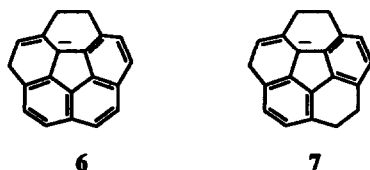
time of the quench. While **6** could result from three-fold protonation of a tetraanion, it could also be produced by complete protonation of an initial dianion by ammonia, followed by monoprotonation of a second dianion. This latter route also explains **7** if the protonation of the second dianion takes place at two different positions. That is, protonation at the 9-position leads to stable monoanion **6**, while protonation at the 5- or 6-position affords a
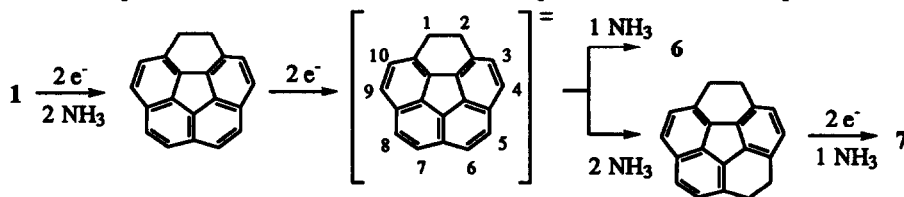
monobenzylic monoanion that protonates quickly leading to a neutral tetrahydro corannulene that rapidly adds two more electrons. Monoprotonation of this new dianion produces **7**.

In conclusion, the calculated results do not lend much support for an anion within an anion structure for the corannulene tetraanion, and this species is either not readily formed in ammonia or does not resist protonation.

REFERENCES AND NOTES

1. (a) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl R. F. and Smalley, R. E. *Nature*, **1985**, *318*, 162. (b) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature*, **1990**, *347*, 354. (c) Kroto, H. W.; Allaf, A. W.; Balm, S. P. *Chem. Rev.*, **1991**, *91*, 1213. (d) Hammond, G. S.; Kuck, V. J., Ed., "Fullerenes," ACS Symposium Series 481, Washington, D.C., 1992. (e) Smalley, R. E. *Acc. Chem. Res.*, **1992**, *25*, 98.

2. Barth, W. E.; Lawton, R. G. *J. Am. Chem. Soc.* **1966**, *88*, 381.

3. Scott, L. T.; Hashemi, M. M.; Meyer, D. T.; Warren, H. B. *J. Am. Chem. Soc.* **1991**, *113*, 7082.

4. See also Borchardt, A.; Fuchicello, A.; Kilway, K. V.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 1921.

5. Janata, J.; Gendell, J.; Ling, C.-Y.; Barth, W.; Backes, L.; Mark, H. B., Jr.; Lawton, R. G. *J. Am. Chem. Soc.* **1967**, *89*, 3056.

6. Ayalon, A.; Rabinovitz, M.; Cheng, P.-C.; Scott, L. T. *Angew. Chem.* **1992**, *31*, 1636..

7. (a) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J.Am.Chem.Soc.*, **1985**, *107*, 3902. (b) Stewart, J. J. P. *QCPE Program No. 455* (Version 5.0).

8. Ab initio calculations were performed using the Gaussian 90 program package: GAUSSIAN90, Revision J. Frish, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzales, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melis, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. *Gaussian, Inc.*, Pittsburg, PA, **1990**.

9. (a) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.*, **1980**, *102*, 939. (b) Gordon, M. J.; Binkley, J. S.; Pople, J.A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.*, **1982**, *104*, 2797.

10. (a) Moller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Binkley, J. S.; Pople, J. A. *Int. J. Quantum Chem.* **1975**, *9*, 229.

11. O'Brien, D.H.; Hart, A.J.; Russell, C.R. *J. Am. Chem. Soc.* **1975**, *97*, 4410.

12. Mulliken population analysis was also carried out with the 6-31G* basis set, and GAPT population analysis[13a] was also performed. However, our test results on trimethylenemethane dianion showed that Mulliken population analysis with the 3-21G basis set gives charge distributions closest in agreement with the more reliable, but computationally demanding, Bader method.[13b,c]

13. (a) Cioslowski, J. *J. Am. Chem. Soc.*, **1989**, *111*, 8333. (b) Bader, R. F. W. *Acc. Chem. Res.*, **1985**, *18*, 9, and references therein. (c) Wiberg, K. B. *J. Am. Chem. Soc.*, **1990**, *112*, 4177.

14. Müllen, K.; Huber, W.; Neumann, G.; Schnieders, C.; Unterberg, H. *J. Am. Chem. Soc.* **1985**, *107*, 801. Müllen, K. *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 204. See also Rabideau, P.W. *Tetrahedron* **1989**, *45*, 1579 and Rabideau, P. W.; Z. Marcinow *Org. React.* **1992**, *42*, 1.

15. Metal-ammonia reductions: Na (0.6-0.8 mmol) was added to anhyd. ammonia-THF (2:1 v/v; 6 mL) at reflux (argon), followed by 1 (0.1 mmol). After 20 min the mixture was pumped (argon pressure) into a large excess of aq. NH_4Cl or MeI-THF solution (inverse quench). Products were purified by flash column chromatography on 230-400 mesh silica gel (Merck) with hexane as eluent.

16. (a) ^{1}H NMR (CDCl$_3$) d 2.21 (m,1H), 2.76 (m,1H), 3.04-3.16 (m,2H), 3.30 (m,1H), 3.68 (m,1H), 4.48 (m,1H), 5.76 (m,1H), 7.08 (dd,2H), 7.50-7.58 (m,4H); ^{13}C NMR (CDCl$_3$) d 27.20, 28.66, 31.67, 44.78, 121.81, 125.05, 125.44, 125.88, 126.06, 129.37, 129.96, 133.79, 134.19, 135.74, 147.97, 150.85; MS m/z 254 (M$^+$); high res. MS: calcd for $C_{20}H_{14}$ 254.1095, found 254.1092 (b) ^{1}H NMR (CDCl$_3$) d 2.23 (m,1H), 2.64-2.70 (m,1H), 2.78-2.84 (m,2H), 2.94-3.00 (m,1H), 3.07-3.15(m,2H), 3.36-3.41(m,2H), 3.48-3.54 (m,1H), 4.22(m,1H), 5.71(m,1H), 6.78-6.95 (m,4H); ^{13}C NMR (CDCl$_3$) d 27.o7, 28.28, 31.43, 45.20, 120.80, 124.59, 124.87, 126.40, 126.56, 129.41, 129,76, 135.04, 135.36, 135.88, 141.64, 141.97, 148.25, 151.55; MS m/z 256 (M$^+$); high res. MS: calcd for $C_{20}H_{16}$ 256.1252, found 256.1254 (c) Reductive monomethylation (GC/MS) gave 2 and 3 (20:80). Complete separation was not possible, but column chromatography allowed enrichment in 3 (92%). Its NMR, similar to 5, is as follows. ^{1}H NMR (CDCl$_3$) d 1.63 (s,3H), 2.26-2.36 (m,1H), 2.60-2.65) (m,1H), 2.73-2.82 (m,2H), 3.01-3.06 (m,2H), 3.14-3.22 (m,1H), 3.31-3.40 (m,2H), 3.55 (m,1H), 5.70 (m,1H), 6.75-6.91 (m,4H). MS m/z 270 (M$^+$).