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Corannulene Tetraanion: A Novel Species with Concentric Anionic Rings

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This is more evident if one looks down the *b* axis of the unit cell of **1** · **3** (in effect, the space between pairs of dimers); then the beautiful packing shown in Figure 3 emerges; the central

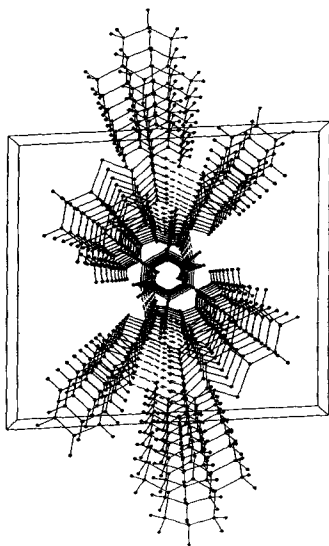


Fig. 3. View down the *b* axis of $(\mathbf{1} \cdot \mathbf{3})_2$ illustrating the highly symmetrical, tunnel-like stacking.

“tunnel” is formed by oxygen atoms of **3**. Interestingly, a hot toluene solution of the adduct $(\mathbf{1} \cdot \mathbf{3})_2$ dissolves solid LiBr, further heating of the resulting solution then causes precipitation of a white solid. The adduct also absorbs appreciable quantities of Br₂ gas to afford a mustard-colored powder. The identities of both products are being investigated.

We are also investigating supramolecular systems with similar components to those described here. To explore further the reasons for the carcinogenicity of **2** and the relative innocuousness of **3**, we are also examining their adducts with individual DNA bases and with natural base pairs.

Experimental Procedure

(1 · 3): 2-aminobenzothiazole (**1**) (3.00 g, 20 mmol) was dissolved at room temperature in a solution of **3** (2.56 g, 20 mmol) in toluene (20 mL). This solution was cooled at 0 °C for 1 d to afford white crystals of the adduct (first batch yield 5.05 g, 91 %; m.p. 101–102 °C; correct elemental analysis; ¹H NMR (CDCl₃, 250 MHz, 25 °C): δ = 7.53–7.44 (m, 2H; **1**), 7.23 (t, 1H; **1**), 7.04 (t, 1H; **1**), 6.33 (br.s, NH₂; **1**), 3.18 (t, 4H; **3**), 2.88 (s, 2CH₃; **3**), 1.95–1.86 (quin, 2H; **3**). Crystals suitable for X-ray analysis were grown slowly from a more dilute solution (5 mmol of each component in 10 mL toluene).

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1 · 3, 144467-83-4.

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- [5] X-ray crystal structure data on (OxNH₂ · DMPU) **1 · 3**: C₁₃H₁₈N₄O₈, *M* = 278.4, monoclinic, space group *C2/c*, *a* = 20.187(18), *b* = 7.535(3), *c* = 18.666(13) Å, β = 92.72(7)°, *V* = 2836.1(14) Å³, *Z* = 8, ρ_{calc} = 1.304 Mg m^{−3}, *F*(000) = 1184, λ(MoKα) = 0.71073 Å, μ(MoKα) = 2.27 cm^{−1}, *T* = 180 K. Data were collected on a Stoe four-circle diffractometer, 2627 reflections collected in range 7° ≤ 2θ ≤ 45°. The structure was solved by a combination of direct methods and Fourier difference techniques, and refined by full-matrix least squares [all non-hydrogen atoms anisotropic; all hydrogens except H(3a), H(3b) placed in idealised positions; H(3a), H(3b), the NH₂ hydrogen atoms of **1**, freely refined] to *R* = 0.082, *R*_w = 0.095 for 1857 unique reflections [*F* > 4σ(*F*)]. Further details of the crystal structure are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, GB-Cambridge, CB2 1EW (UK), by quoting the full journal citation.
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Corannulene Tetraanion: A Novel Species with Concentric Anionic Rings**

By Ari Ayalon, Mordecai Rabinovitz,* Pei-Chao Cheng, and Lawrence T. Scott*

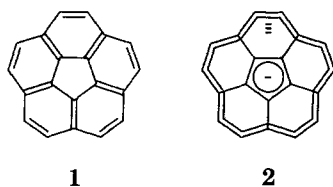
Dedicated to Professor Emanuel Vogel and Professor Klaus Hafner on the occasion of their 65th birthdays

Tetraanions of polycyclic aromatic hydrocarbons have only rarely been observed.^[1] The possibility that corannulene (**1**) might be easily reduced and even “supercharged” with four electrons to make a stable, closed-shell tetraanion, however, was suggested by the prediction^[2] that the lowest unoccupied molecular orbital (LUMO) of this unique bowl-shaped molecule should be doubly degenerate and lie below the antibonding energy level (*E*_{LUMO} = −0.922 eV by MN-DO calculations). The prospect that the tetraanion of corannulene might enjoy special stability as an aromatic cyclopentadienyl anion (6e/5C) suspended by five radial bonds within the hole of an aromatic 18e/15C annulenylium trianion as in **2** provided additional impetus to examine this system, since such a species might fulfill the long quest for a π-electron system having concentric aromatic rings, which began with the heroic synthesis of kekulene.^[3] Herein we report the preparation, ¹H and ¹³C NMR spectra, and proton quenching experiments of the corannulene tetraanion.

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Reduction of corannulene (**1**)^[4] at -78°C with excess lithium metal in $[\text{D}_8]\text{THF}$ over a period of several days leads to a series of three color changes, first to green, then to purple, and finally to brownish-red. Only for the last stage could an NMR spectrum be recorded, presumably owing to the presence of paramagnetic species at the intermediate stages of reduction.^[5] Quenching this solution with water affords tetrahydrocorannulene (GC/MS, m/z 254) as the major product accompanied by lesser amounts of dihydrocorannulene and corannulene (ratio $\approx 4:2:1$). The formation of tetrahydrocorannulene upon protonation constitutes one piece of evidence for the presence of a quadruply charged system.

Further evidence that the final reduction product is indeed a tetraanion comes from its ^{13}C NMR spectrum: ($[\text{D}_8]\text{THF}$) $\delta = 86.8$ (d, $^1J_{\text{CH}} = 151$ Hz, rim CH), 95.1 (tt \approx heptet, $^3J_{\text{CH}} = 7.0$ Hz, $^2J_{\text{CH}} = 3.6$ Hz, rim quaternary C),^[6] 112.4 (m, $^3J_{\text{CH}}$ and two different $^4J_{\text{CH}}$, hub C). All three ^{13}C NMR bands of the reduction product are dramatically shifted to high field compared to those of the neutral hydrocarbon (cf. **1**: $\delta = 127.9, 132.3, 136.9$, respectively, in $[\text{D}_8]\text{THF}$); the weighted center of the ^{13}C NMR bands shifts by $\Delta\delta = -36.1$. Charge/chemical shift correlations first proposed by Fraenkel et al.^[7a] predict a total ^{13}C NMR signal shift of $\Delta\delta \approx 160$ per negative charge. A subsequent modification of this correlation introduced by Eliasson, Edlund, and Müllen,^[7b] which takes into account the anisotropy of π -electron systems, predicts a shift of $\Delta\delta \approx 150$ per unit of charge. The actual value we observe is $\Sigma\Delta\delta = 722$ (!) or $\Delta\delta = 180.5$ per unit of charge. These correlations provide convincing evidence that the species observed is a quadruply charged system.

The ^1H NMR spectrum of the corannulene tetraanion in $[\text{D}_8]\text{THF}$ consists of a single line at $\delta = 6.95$ (cf. **1**: $\delta = 7.93$ in $[\text{D}_8]\text{THF}$). This low-field chemical shift is surprising in view of the high electron density on the rim methine carbon atoms (see ^{13}C NMR data and charge density calculations). Ordinarily, protons attached to anionic hydrocarbon C atoms are strongly shielded and resonate at exceptionally high field, for example, in the pentadienyl anion $\delta_{\text{avg}} = 4.0$.^[8] Apparently, the π system of the corannulene tetraanion supports an induced diamagnetic ring current (or two) that is strong enough to counterbalance the shielding effect of four negative charges.

Whether or not the "annulene-within-an-annulene" structure **2** is the best description of this tetraanion remains to be established. MNDO calculations, with the lithium ions included,^[2] yield a global minimum in which all four lithium ions lie on the convex face of a bowl-shaped tetraanion, each located over the face of a different benzene ring. This structure has 1.1 units of negative charge on the five hub carbon atoms, 2.2 units of negative charge on the ten rim methine carbon atoms, and 0.7 units of negative charge on the five rim quaternary carbon atoms. The five radial bonds of the tetraanion are calculated to be $0.01\text{--}0.06$ Å longer than the five C–C bonds within the inner ring, as one would expect for **2**. High-level theoretical calculations on all the reduced (and oxidized) states of corannulene would be most desirable;^[9] however, it is already clear from the initial results reported

herein first that corannulene can be easily reduced to a stable tetraanion, and second that this tetraanion carries substantial negative charge on both the hub and the rim carbon atoms, thereby classifying it as a species with concentric anionic rings.

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1, 5821-51-2; **2** $\cdot 4\text{Li}^+$, 144467-82-3.

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Towards Artificial Ion Channels: Transport of Alkali Metal Ions across Liposomal Membranes by "Bouquet" Molecules**

By Marko J. Pregel, Ludovic Jullien, and Jean-Marie Lehn*

Transmembrane ion transport is essential to living systems and is involved in vital processes such as energy metabolism and the excitability of nerve and muscle.^[1] Transport may take place by mechanisms involving either diffusive carrier (shuttle) or membrane-spanning channel (pore) species.^[2] In the field of supramolecular chemistry, free carrier processes have been actively investigated for many years.^[3] More recently the design, synthesis, and study of molecular assemblies capable of transporting ions across membranes by the channel mechanism has been a subject of increasing inter-

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