Stable High-Order Molecular Sandwiches: Hydrocarbon Polyanion Pairs with Multiple Lithium Ions Inside and Out

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Stable ten-component sandwich compounds have been characterized in which four lithium ions reside between two tetraanions derived from corannulene or its alkyl-substituted derivatives and four additional lithium ions decorate the exterior. In tetrahydrofuran solution, the four lithium ions inside the sandwich can exchange environments with the four external lithium atoms, but the two tetraanion decks of the sandwich never separate from one another on the time scale of nuclear magnetic resonance. Theoretical calculations point to a "stacked bowl" conformation and a low energy barrier for synchronous double inversion of the tetraanion bowls in the solvated sandwich compounds.

Lithium derivatives of conjugated hydrocarbon dianions exist preferentially as "ion triplets," with the lithium cations located on opposite faces of the dianion (*1*), and inverted ion triplets with a single lithium ion sandwiched between two organic anions are likewise known (*2, 3*); however, higher order aggregates in which multiple lithium ions bind two hydrocarbon polyanions together as stable sandwich dimers in solution are exceedingly rare (*4, 5*). We descibe in this report several complex sandwich dimers wherein tetraanions of corannulene and its derivatives (Fig. 1) constitute the two "decks" of the dimers and eight lithium ions distribute themselves above, below, and between the decks (Fig. 2). The dimers in this class of molecular aggregates are strongly bound and do not dissociate to tetraanion monomers on the nuclear magnetic resonance (NMR) time scale in tetrahydrofuran (THF) solution at room temperature.

Corannulene (*6–8*), with its bowl-shaped equilibrium geometry (*9*), represents the minimum subunit of C_{60} and the higher fullerenes that retain a curved molecular surface. Earlier studies on the tetraanion of corannulene (*10*) gave no clues that corannulene^{4-} with 4 Li^+ might exist as a dimer (corannulene^{4-}/4Li^+)$_2$: The ^1H NMR spectrum of the parent species consists of a single line, and the ^{13}C NMR spectrum shows only three signals, the chemical shifts of which reflect the delocalization of four extra electrons in the π system over all 20 carbon atoms of the tetraanion (*11*).

The first evidence for formation of dimers of corannulene^{4-}/4Li^+ came from studies on corannulene derivatives. Owing to their lower symmetry, the dimers of monosubstituted corannulene tetraanions would be expected to exhibit supramolecular stereochemistry, a meso dimer and a *d,l* dimer (Fig. 3) being formed with almost equal probability. Indeed, reduction of *tert*-butylcorannulene (*12*) with excess lithium metal in THF-d_8, under the conditions previously described for reduction of unsubstituted corannulene (*10, 13*), gives not one but two species in similar but unequal abundance, as revealed by ^{13}C and ^1H (both one- and two-dimensional) NMR spectroscopy. Two sets of very similar peaks, some of which coincide, can be seen in both spectra [Fig. 4A and (*11*)]. Particularly telling are the two lowest field singlets in the ^1H NMR spectrum (chemical shift δ 7.34 and 7.33) that arise from resonance of the protons ortho to the *tert*-butyl groups in the major and minor species, respectively. Reduction of isopropylcorannulene (*14*) with excess lithium metal under the same conditions likewise gives two species in similar but unequal abundance (*11*). In this case, as expected, the two methyl groups in each isopropyl substituent are diastereotopic, so each species gives rise to two methyl hydrogen doublets in the ^1H NMR spectrum, even at room temperature.

Compelling evidence that these species are all dimers of the sort depicted in Fig. 3 comes from the successful detection of a "mixed dimer" between corannulene^{4-}/4Li^+ and *tert*-butylcorannulene^{4-}/4Li^+ (R = H on one deck, and R = *tert*-butyl on the other). In this experiment, we recorded the ^1H NMR spectrum of a 5:1 mixture of unsubstituted corannulene and *tert*-butylcorannulene that had been reduced with excess lithium metal (Fig. 4B). Under the conditions used, self-dimerization of unsubstituted corannulene^{4-}/4Li^+ is stoichiometrically favored, and this product gives rise to the dominant singlet at δ 7.01. Conversely, the meso and *d,l* self-dimers of *tert*-butyl corannulene^{4-}/4Li^+ (described above) are stoichiometrically disfavored in this experiment, and their NMR signals hardly appear above the baseline. The new NMR signals in Fig. 4B that cannot be

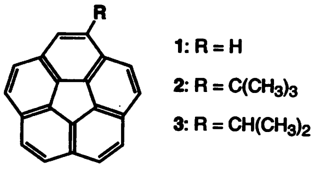

Fig. 1. Corannulene (**1**), *tert*-butylcorannulene (**2**), and isopropylcorannulene (**3**).

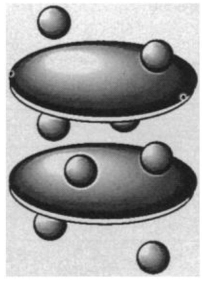

Fig. 2. Formal representation of the side view of dimers from two corannulene tetraanions (disks) and eight lithium cations (balls).

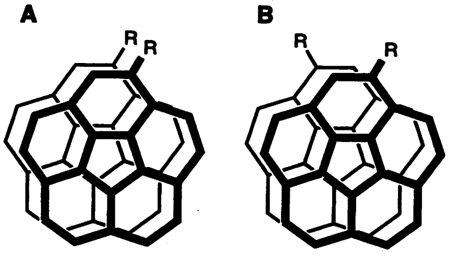

Fig. 3. Stereoisomeric dimers of tetraanions derived from a monosubstituted corannulene (lithium cations omitted for clarity): (**A**) meso dimer and (**B**) *d,l* dimer. In-plane rotation of one tetraanion deck with respect to the other is expected to be facile but will not interconvert (A) and (B).

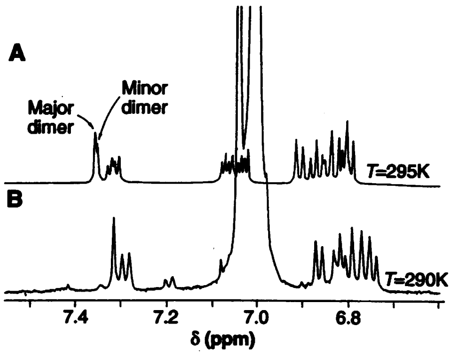

Fig. 4. Low-field portion of the ^1H NMR spectrum resulting from lithium metal reduction of (**A**) pure *tert*-butylcorannulene and (**B**) a 5:1 mixture of unsubstituted corannulene and *tert*-butylcorannulene. The chemical shift δ is defined to be in parts per million (ppm).

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attributed to self-dimers of either tetraanion consist of (i) a low-field singlet at δ 7.31, which arises from the proton ortho to the *tert*-butyl group in the mixed dimer, (ii) a large singlet at 7.05, which arises from the 10 equivalent protons on the unsubstituted corannulene deck of the mixed dimer, and (iii) a series of doublets assigned to the remaining protons on the *tert*-butylcorannulene deck of the mixed dimer.

The ^{7}Li NMR spectroscopy provided further support for the dimeric nature of these species and indicated that the equilibrium arrangement of the cations therein has four lithium ions sandwiched between the two tetraanion decks of the dimer and the other four ions located symmetrically (on the NMR time scale) outside (Fig. 2). Thus, unsubstituted corannulene^{4-}/4Li$^+$, which is now proposed to exist as a dimer, gives rise to two signals of equal intensity in its ^{7}Li NMR spectrum at 210 K in THF-d_8 (LiBr in THF was used as the external standard); one very broad band appears at δ −4.5, and a much narrower band appears at δ −11.7. The unusually high field shifts of both ^{7}Li absorption lines are a consequence of the strong shielding of all the lithium ions by the diamagnetic ring currents of the aromatic corannulene tetraanions. Such shielding occurs if the nuclei under study are located directly above or below the anisotropic π-delocalized ring (*2, 15*).

When approximately two equivalents of LiBr were added to the THF-d_8 solution, no ^{7}Li NMR peak for LiBr (δ 0.0) appeared in the spectrum, and the peak at δ −4.5 also disappeared. In their place, a new peak appeared at about δ −2.5, and the peak at δ −11.7 remained unaffected. These observations show that the signal at δ −11.7, which was not influenced by addition of the common ion, comes from lithium cations that are intimately bound to the anionic corannulene moiety [contact ion pairs (CIP)], and the peak at δ −4.5 can be attributed to more loosely bound solvent-separated lithium cations (SSIP), which undergo a rapid exchange process with the added LiBr. Because the "interior" lithium ions in dimers of the sort pictured in Fig. 2 ought to feel the combined magnetic shielding influence of both aromatic decks (*2, 15*) and could also be expected to resist exchange with external LiBr, the ^{7}Li NMR signal at δ −11.7 can be reasonably assigned to the four lithium ions sandwiched between the two anion decks. The exchangeable "exterior" lithium ions, then, are responsible for the signal at δ −4.5.

When the NMR sample of unsubstituted corannulene^{4-}/4Li$^+$ dimer (without added LiBr) is warmed to room temperature, the two ^{7}Li NMR lines at δ −4.5 and −11.7 coalesce into a single peak at δ −8.1 (coalescence temperature T_c = 265 K) (Fig. 5). Thus, the interior and exterior lithium ions of the dimer are able to exchange places with one another. The energy barrier ($\Delta G^\ddagger$) associated with this dynamic process is calculated from the NMR data to be 13.2 kcal/mol at 265 K. The isopropyl- and *tert*-butyl–substituted corannulene^{4-}/4Li$^+$ dimers show analogous ^{7}Li NMR spectra (*11*) that likewise coalesce upon warming.

The ^{13}C and ^{1}H NMR spectra of the substituted corannulene tetraanions show no evidence for interconversion of the stereoisomeric dimers, even at room temperature under conditions where their ^{7}Li NMR spectra have collapsed to a single peak. Thus, the scrambling of lithium ions between the interior and exterior environments must occur rapidly without dissociation of the dimers to monomeric corannulene^{4-}/4Li$^+$ species.

Although the geometry of the corannulene components in these dimers cannot be gleaned from NMR experiments, because the two faces of each corannulene tetraanion are already rendered nonequivalent by the structures of the dimers, semiempirical MNDO (modified neglect of diatomic overlap) molecular orbital calculations (*16*) clearly favor a "stacked-bowl" geometry (convex face to concave face) as the global energy minimum for the parent aggregate of two corannulene^{4-} and 8 Li$^+$ (Fig. 6). The alternative concave-concave and convex-convex dimers are both calculated to relax with no energy barrier to this convex-concave conformation, as is the dimer with planar decks.

One obvious problem with the "stacked-bowl" picture is its seeming incompatibility with the observed equivalence of the four exterior lithium ions (^{7}Li NMR) and with the observed equivalence of the two tetraanion partners in each dimer (^{13}C and ^{1}H NMR). Rapid intermolecular exchange of the four exterior lithium ions (SSIP) could reasonably explain the apparent equivalence of the two lithium ions in the top bowl with those outside the bottom bowl of these convex-concave dimers. To explain the equivalence of the top and bottom corannulene bowls themselves, however, it is necessary to propose a rapid bowl-to-bowl inversion of both corannulene decks (*17*). The MNDO calculations predict an activation enthalpy of 13.4 kcal/mol for concerted bowl-to-bowl inversion of the two corannulene decks in the unsubstituted system, but such a high barrier is clearly inconsistent with the NMR spectra, which show no evidence for freezing out such a dynamic process even at 190 K. Of course, the calculations do not take solvation into account, and solvation of the exterior lithium ions might significantly change the energetics of the inversion.

To address this aspect of the problem, we removed all four exterior lithium ions and carried out single-point energy calculations (without geometry reoptimization) on both the "stripped" convex-concave dimer and its transition state for concerted double inversion. In this hypothetical 2(corannulene^{4-})/4Li$^+$ aggregate that retains only its interior lithium ions, the barrier to concerted double inversion drops from 13.4 kcal/mol to only 0.8 kcal/mol at the MNDO level of theory. It appears safe to conclude, therefore, that solvation greatly lowers the inversion barrier and that the double inversion is probably fast on the NMR time scale.

Although corannulene and its derivatives are characterized by unusual curvature, there is reason to suspect that some polyanions of planar hydrocarbons form analogous aggregates. The dimers of the corannulene tetraanion escaped detection until studies were performed on derivatives with sufficiently low symmetry to exhibit supramolecular stereochemistry, and the same strategy may help to uncover dimers involving planar systems.

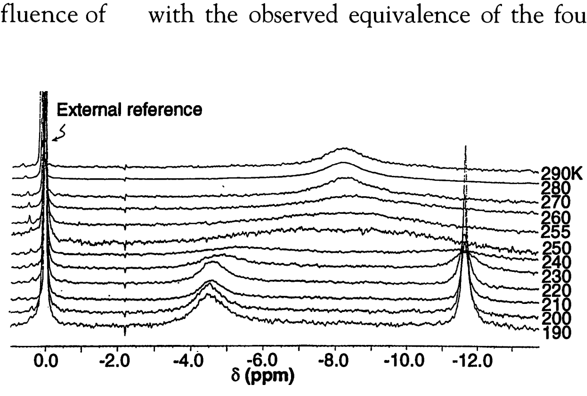

Fig. 5. Variable-temperature ^{7}Li NMR spectrum of the corannulene^{4-}/4Li$^+$ dimer in THF-d_8. Each trace is labeled with a temperature in kelvin. The external reference is LiBr in THF.

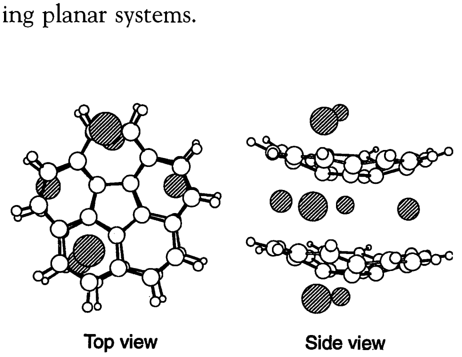

Fig. 6. Minimum-energy geometry calculated (MNDO) for the corannulene^{4-}/4Li$^+$ dimer. Lithium ions are shaded.

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11. The NMR data of compounds **1**, **2**, and **3** and their tetraanions in THF-d_8. The ^{1}H and ^{13}C data are in parts per million downfield from TMS, and the ^{7}Li data are in parts per million downfield relative to LiBr (0.01M LiBr in THF as external reference). The ^{1}H and ^{13}C spectra were recorded on a Bruker AMX-400 spectrometer with a ^{2}H lock. The THF-d_7 low-field proton band was used for calibration of ^{1}H spectra (δ 3.67); the THF-d_8 ^{13}C low-field signal served for calibration of the ^{13}C spectra (δ 67.7). For anionic species, ^{1}H chemical shifts varied as much as ±0.03 ppm from one sample to the next. Abbreviations: (s) singlet, (d) doublet, (m) multiplet, and (AB) AB quartet. Compound **1**: ^{1}H: 7.93 (s); ^{13}C: 127.9, 132.3, 136.9. Compound **1**$^{4-}$: ^{1}H: 6.98 (s); ^{13}C: 86.8, 95.1, 112.4; ^{7}Li (210 K): −4.5 (4 Li), −11.7 (4 Li). Compound **2**: ^{1}H: 8.40 (d, 1 H), 7.95 to 7.86 (m, 8 H); 1.80 (s, 9 H); ^{13}C: 33.4, 38.1, 123.4, 127.0, 127.7, 127.8, 128.0, 128.1, 128.14 (2 C), 129.0, 130.5, 131.5, 132.0, 132.2 (2 C), 135.6, 136.5, 136.7, 137.1, 137.3, 151.3. Compound **2**$^{4-}$: ^{1}H: 2.4 (s, 9 H), [6.77 (d), 6.77 (d), 7.78 (d), 7.79 (d), 6.81 (d), 6.83 (d), 6.84 (d), 6.86 (d)] (4 H), 6.89 (d, 1 H), [7.01 (d), 7.02 (d)] (1 H), [7.04 (d), 7.05 (d)] (1 H), [7.29 (d), 7.31 (d)] (1 H), [7.33 (s), 7.34 (s)] (1 H); ^{13}C: 33.13, 33.15, 39.15 (2 C), 83.79 (2 C), 84.60, 84.73, 84.92, 85.08, 85.16, 85.27, 86.86, 86.87, 88.34 (2 C), 88.56, 88.91, 89.88, 89.89, 93.02, 93.12, 94.25, 94.31, 94.36, 94.51, 95.56, 95.68, 95.78, 95.84, 96.90, 96.94, 108.08, 108.09, 112.24 (2 C), 112.38 (2 C), 112.47, 112.53, 112.82 (2 C), 112.91 (2 C); ^{7}Li (210 K): −5.0 (4 Li), −11.7 (4 Li). Compound **3**: ^{1}H (190 K): 1.41 (d, 3 H), 1.77 (d, 3 H), 3.95 (m, 1 H), 7.89 (d, 1 H), 7.95 to 8.06 (m, 7 H), 8.22 (d, 1 H); ^{1}H (295 K): 1.61 (d, 6 H), 3.91 (m, 1 H), 7.80 (s, 1 H), 7.87 to 7.97 (m, 7 H), 8.14 (d, 1 H); ^{13}C (297 K): 24.8, 31.5, 122.8, 125.9, 127.7, 127.9, 128.1 (overlapping peaks), 131.2, 131.7, 131.9, 132.3, 132.8, 135.8, 136.9, 137.1, 137.4, 149.2. Compound **3**$^{4-}$: ^{1}H (230 K): 1.58 (d, 3 H), 1.63 (d, 3 H), 2.5 (d, 6 H), 4.56 (broad, 2 H), [6.88 (d), (6.89, 7.08) (AB), (6.91, 6.71) (AB), 6.70 (d)] (6 H), [6.84 (d), 6.86 (d)] (2 H), [6.89 (d), 6.91 (d)] (2 H), [6.97 (d), 6.99 (d)] (2 H), [(7.06, 7.075) (AB), (7.07, 7.09) (AB), 7.095 (s), 7.10 (s)] (6 H); ^{13}C (297 K): 25.4, 26.1, 35.0, 35.1, 84.0, 84.5, 84.9, 85.0, 86.1, 86.3, 86.4, 88.3, 88.8, 88.9, 90.0, 94.5, 95.0, 96.0, 96.2, 108.8, 111.4, 111.7, 111.8, 113.1, 113.4; ^{7}Li (210 K): −3.3 (4 Li), −11.7 (4 Li).
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Electromagnetic Heating in the Early Solar Nebula and the Formation of Chondrules

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Certain opaque inclusions within primitive meteorites exhibit textures that suggest chondrules formed during intense, short-duration radiative heating episodes in the early solar system. Experimental support for this interpretation is provided by the textures produced when chondrule-like assemblages are heated with visible laser light. Computer simulations of radiative heating provide additional evidence for the role of electromagnetic energy in heating nebular solids by offering an explanation for the size distributions of chondrules and the presence of dusty chondrule rims. Nebular lightning and magnetic reconnection flares are possible sources of electromagnetic energy for these transient heating events.

Chondrites, which account for ~85% of the meteorites that fall to Earth, are characterized by the presence of chondrules, millimeter-sized silicate-rich objects whose textures and spherical shapes suggest that they cooled rapidly from molten droplets floating freely in space (*1–3*). A growing body of evidence suggests that chondrules formed within the solar nebula from preexisting aggregates of dust (*2*). However, a consensus is lacking as to what was responsible for melting these aggregates, leaving an important gap in our knowledge of the processes at work during the earliest stages of the solar system's formation. Current theories include frictional heating of dust during infall into the solar nebula (*4*, *5*), radiative heating during a T-Tauri phase of the sun (*6*), and heating through collisions with energetic particles produced in electrostatic discharges (lightning) (*7–10*) or magnetic reconnection flares (*10–12*). In this report, textural evidence within chondrules is described that suggests visible and near-infrared radiation played an important role in chondrule formation. Computer simulations demonstrate how the size distributions of chondrules and dusty chondrule rims can be explained as products of radiative heating.

Chondrules mainly consist of olivine $[(Mg,Fe)_2SiO_4]$ and pyroxene $[(Mg,Fe)SiO_3]$, which absorb little energy in the visible and near-infrared region of the electromagnetic (EM) spectrum (~0.4 to 10 μm). In contrast, opaque inclusions of troilite (FeS), pentlandite $[(Ni,Fe)_9S_8]$, magnetite (Fe_3O_4), and Ni-, Fe-rich metal within chondrules readily absorb energy in this frequency range. The opaque minerals in some chondrules occur as unique, fluffy assemblages (Fig. 1A). These fluffy opaque inclusions (FOIs) are typically ~10 to 50 μm in diameter and consist of clusters of individual troilite or pentlandite grains with interstitial olivine or pyroxene. Rarer examples include magnetite or Ni-, Fe-rich metal as the opaque phase. Compositionally, FOIs are nearly identical to compact opaque mineral inclusions within chondrules (Fig. 1B). They differ only in that the enclosing silicate in FOIs is also intimately intermixed with the opaque phase, rather than simply surrounding it (*13*).

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