Stable Tetraanionic Carbon Tubes

Picotube Tetraanion: A Novel Lithiated Tubular System**

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Carbon nanotubes have attracted considerable attention since their discovery,[1] and have recently been the focus of intensive investigations. Studies have revealed that nanotubes exhibit extraordinary electronic properties.[2,3] Nanotubes have been shown to ignite upon exposure to short-range flashes of light,[2] and recently ultrafast carbon-nanotube-based transistors have been shown to outperform their silicon counterparts.[3]

The electronic and magnetic properties of such tubes might be studied with guest atoms present inside the tube, such as in fullerenes.[4] However, standard nanotubes, as well as fullerenes, are highly insoluble in most solvents, which makes such studies rather intricate. Additionally, nanotubes are end-capped, and the insertion of atoms or cations into the tube is very difficult. The conjugated tubelike polycyclic aromatic hydrocarbon (PAH) 5,24:6,11:12,17:18,23-tetra[1,2]-benzenotetрабензо[a,e,i,m]cyclohexadecene (1), dubbed “picotube”,[5] has successfully been synthesized in gram amounts through the dimerization metathesis of tetradihydrodianthracene.[6a]

Picotube 1 possesses open ends and is more soluble than standard nanotubes. In addition, its nanotube-like structure and fullerene-like ability to include endohedral atoms makes it an ideal candidate for further study. The picotube could play a role as a host molecule, by encapsulating one or more counterions upon charging, while possibly coordinating with others on the exterior. The specific orientation of such cations could also reveal information regarding the charge distribution within the molecule.

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.
Picotube 1 has been fully characterized by NMR spectroscopy, mass spectrometry, density functional theory (DFT) calculations, matrix IR spectroscopy and crystal structure analysis.

The latter reveals that the picotube, which consists of four anthracene units, has a diameter of 5.4 Å and a length of 8.2 Å, and shows $D_{4h}$ symmetry for the neutral species 1. However, DFT calculations and low-temperature IR studies indicate that the $D_{4h}$ symmetry is only a time-averaged structure of two rapidly interconverting $D_{2d}$ isomers (Figure 1), obtained by twisting of the quinoid double bonds.

This lowering of symmetry has been calculated to provide an energy gain of about 4.5 kcal mol$^{-1}$, relative to $D_{4h}$ symmetry.

$^1$H and $^{13}$C NMR spectroscopy show that picotube 1 indeed possesses $D_{4h}$ symmetry on the NMR timescale, with only one AA'BB' pattern in the proton spectrum and four resonances in the carbon spectrum (Figure 2a). Previously, the freezing of conformational movement could not be observed down to 203 K, and in the present study, no splitting of the signals was seen, even at 150 K, which indicates that the barrier for topomerization of the neutral molecule is lower than 7.8 kcal mol$^{-1}$.

In view of the interest in introducing alkali metals into nanotubes, we report that the picotube undergoes slow chemical reduction by lithium metal to form an unusually stable charged species. The $^1$H NMR spectrum of the light-yellow neutral species tends to broaden as the solution becomes olive green. The spectrum loses its form as the solution further changes color, first to dark green, and then to dark blue, most likely as a result of the formation of paramagnetic species. Finally a dark-brown solution is obtained which gives a different $^1$H NMR spectrum (Figure 2b) to that of the neutral species. Since the olive-green solution must contain a species that has, at least, been reduced to a radical anion, and the dark-blue solution contains a dianionic species, then the diamagnetic dark-brown solution must contain a species which can be no less reduced than a tetraanion. Charge-density calculations from $^{13}$C NMR spectroscopy show a value for $\mathcal{K}$ of approximately 131 ppm per electron, in accordance with the formation of a quadruply charged species.

DFT calculations using gauge-including atomic orbitals (GIAO) also reinforce the assessment that the reduced species is a tetraanion (see below).

No diamagnetic species were observed until the formation of the tetraanion, and further attempts at reduction failed to yield new products. The dianion is, therefore, likely to be an easily reduced triplet diradical or unstable singlet. The tetraanion was fully characterized by NMR spectroscopy, and charge-density calculations support its nature. According to the $^1$H NMR spectrum, quenching of the tetraanion with oxygen leads to the near quantitative and immediate recovery
of the neutral compound, which indicates that no bonds are formed or cleaved during the reduction process.

In contrast to the neutral compound, the tetraanion gives more complex spectra, with eight proton signals and fourteen carbon lines observed (Figure 2b). The picotube is thus reduced to a species with lower symmetry (C$_2$v, C$_0$ or D$_2$). The proton signals are found in two groups, and can be shown to be representative of one system, the anthracenic unit. Each hydrogen and carbon atom of any given anthracene unit is different, and gives a characteristic resonance; bond cleavage would result in a different number of proton and carbon signals. The very fast dynamic motion, which is only detectable by matrix IR spectroscopy in the neutral compound, slows down dramatically in the charged species. The tetraanion shows no coalescence of signals, even at 325 K. This result means that the barrier of the “double bonds”[19] and bridge the sp$^2$ carbon atoms. The remaining two olefin units are uncoordinated according to the experimental data (charge alternation). Because of the small size of the cavity, coordination is only possible from outside the tube. The remaining two Li atoms are located so as to interact with the aromatic systems, either outside or inside the tube. A systematic DFT study[21] of numerous conceivable geometries was performed to find the optimum location of the other two Li atoms, which led to a global minimum of C$_2$ symmetry, with two Li atoms positioned inside the tube, separated by 2.61 Å. The endohedral Li atoms coordinate to the double bonds that are already coordinated by Li$^+$ ions from outside the tube, to form doubly bridged ethylene units that are analogous to the 1,2-dilithioethane structure investigated by Schleyer and Pople.[18a] A similar structure has been observed in a stilbene–dilithium complex.[18c] An even stronger interaction (C–Li 2.14 Å) was found with the ipso carbon atom of a neighboring benzene ring. Our theoretical finding that two of the Li atoms are bound inside the tube is further supported by an X-ray structural analysis of the picotube–Ag$^+$ complex (1:2 stoichiometry), in which two Ag$^+$ ions occupy similar positions inside the tube[18d] as were found for Li$^+$ ions in our calculations. Structures investigated with four Li atoms either all outside or inside the tube were all found to be considerably less stable than the above C$_2$ structure. According to the calculations, the C$_2$ structure undergoes a fast racemization to give a time-averaged $D_2$ structure.

The proposed structure is corroborated by a comparison of the theoretically calculated and experimental $^{13}$C NMR spectra of the time-averaged $D_2$ structure (Figure 5). The calculations[10] confirm the large variance between the carbon atoms in the 9 and 10 positions, and predict an even larger difference in $\Delta \delta$ than found by experimentation. All other shifts agree within the error limit of the method (Table 1). The large deviation between theory and experiment of almost 25 ppm for the anionic centers (position 9) can be accounted for by solvation of the coordinated Li ions. While the Li atoms inside the tube are shielded from the solvent, the

![Figure 3. Charge distribution within a) the anthracenylidene units of 1 and b) the anthracene dianion[17], as calculated from $^{13}$C NMR chemical shifts. Filled circles represent negative charge; hollow circles represent positive charge.](image)

![Figure 4. Charge alternation throughout the tetraanion.](image)
Table 1: Calculated (B3LYP/6-31G*, GIAO) and experimental $^{13}$C NMR shifts of the tetraanion.

<table>
<thead>
<tr>
<th>Carbon No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
</tr>
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<tbody>
<tr>
<td>Experimental&lt;sup&gt;[a]&lt;/sup&gt;</td>
<td>118.1(11)</td>
<td>123.7(7)</td>
<td>106.6(13)</td>
<td>123.0(8)</td>
<td>128.4(6)</td>
<td>107.7(12)</td>
<td>121.8(9)</td>
<td>121.6(10)</td>
<td>85.0(14)</td>
<td>143.3(1)</td>
<td>139.9(3)</td>
<td>129.4(5)</td>
<td>131.1(4)</td>
<td>141.9(2)</td>
</tr>
<tr>
<td>Calculated&lt;sup&gt;[a,d,e]&lt;/sup&gt;</td>
<td>111.3(12)</td>
<td>120.9(9)</td>
<td>110.6(13)</td>
<td>125.8(6)</td>
<td>121.3(7)</td>
<td>112.5(11)</td>
<td>121.3(8)</td>
<td>119.4(10)</td>
<td>60.3(14)</td>
<td>140.2(1)</td>
<td>133.0(2)</td>
<td>126.8(5)</td>
<td>129.5(4)</td>
<td>131.0(3)</td>
</tr>
<tr>
<td>Deviation [%]&lt;sup&gt;[f]&lt;/sup&gt;</td>
<td>5.8</td>
<td>2.3</td>
<td>3.7</td>
<td>2.2</td>
<td>5.5</td>
<td>4.3</td>
<td>0.6</td>
<td>1.8</td>
<td>29.1</td>
<td>2.2</td>
<td>4.6</td>
<td>2.0</td>
<td>1.2</td>
<td>7.7</td>
</tr>
<tr>
<td>Rank Deviation&lt;sup&gt;[g]&lt;/sup&gt;</td>
<td>1</td>
<td>2</td>
<td>0</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
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<sup>[a]</sup> In ppm, relative to TMS.  
<sup>[b]</sup> In [D$_8$]THF, at 220 K.  
<sup>[c]</sup> Rank order for experimental and calculated values: 1–14 = lowest-to-highest field.  
<sup>[d]</sup> B3LYP/6-31G* optimized GIAO single-point calculation.  
<sup>[e]</sup> Averaged values for two independent anthracene units (see Supporting Information).  
<sup>[f]</sup> Deviation between experimental and calculated values.  
<sup>[g]</sup> Difference in experimental and calculated ranks.

Figure 5. Computer-generated optimized structure of the picotube$^+$ / 4 Li$^+$ complex at the B3LYP/6-31G* level, with black spheres representing the Li$^+$ cations. All Li–C distances shorter than 2.4 Å are indicated as dashed lines.

The conformational change could arise by small movements of two opposing anthracene units with respect to each other, rather than a concerted movement of all four units in the "$D_2$" equilibrium. The reduction in symmetry during the charging process is most probably a result of charge localization by the Li$^+$ counterions. Carbanions with Li$^+$ counterions are anything but free anions.$^{[22]}$ The C–Li bond may have a partial covalent character. $^7$Li NMR indicates two different lithium cations, with a sharp signal at $\delta = -3.6$ ppm and a broader signal at $\delta = 0.2$ ppm (at 220 K). The latter signal may be attributed to a lithium cation that is externally coordinated to the picotube, while the former attests to another type, located within the tube.$^{[23]}$ Support for this type of structure can be gained from calculations.$^{[12]}$

By summarizing, a host molecule in a stable tetraanionic state has been prepared that can host two Li$^+$ cations within the inner domain of a “tube-like” system resembling the edges of an open nanotube; this anion exhibits a lower symmetry than the neutral molecule. The change from a $D_2$ dynamic process in the neutral system to a $C_2$ equilibrium in the tetraanion is mainly caused by coordination of Li atoms$^{[24]}$ to the inner “walls” of the tube.

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This parameter has been empirically shown to correlate between the total change in chemical shift of the $^{13}$C NMR spectrum upon charging, $\Delta \delta$, and the total extra charge added to the system of the molecule upon charging, $\Delta \mu_{\text{el}}$, as expressed in the equation: $\Delta \delta = K \Delta \mu_{\text{el}}$. In our case, $\Delta \delta = 524$ ppm. For a review, see: a) S. Braun, H.-O. Kalinowski, S. Berger, 150 and More Basic NMR Experiments: A Practical Course, VCH-Wiley, Weinheim, 1998; b) R. Schaefer, W. G. Schneider, Can. J. Chem. 1963, 41, 966; c) H. Spiesecke, W. G. Schneider, Tetrahedron Lett. 1961, 468; d) P. C. Lauterbur, J. Am. Chem. Soc. 1961, 83, 1838; e) P. C. Lauterbur, Tetrahedron Lett. 1961, 274.


[12] All structures were optimized at the B3LYP/6-31G* level of theory within the corresponding point group, and confirmed by harmonic frequency analysis to be either minima or transition states. NMR shifts were calculated using the GIAO method. An extensive investigation of the energy hypersurface using the semiempirical PM3 method preceded the DFT calculations.

[13] a) Using standard 2D NMR techniques, that is, COSY, NOESY, HSQC, HSQC-CSI, and HMBC, b) Clear NOE signals pertaining to carbon pairs 4 and 5, as well as 1 and 8, dismissed the possibility that the alternation is in a neutral-negative-neutral-negative fashion. A structure of two neutral anthracene units alternating with two anthracene dianion units is also possible, which gives the same symmetry. However, DFT calculations confirm the proposed structure, rather than this possibility.

[14] Quotation marks indicate that the dynamic process still exists in the tetraanion, although it is too slow to observe.

[15] Deduced from the Eyring equation, $\Delta G^* = -RT \ln(k/T)$; $k = 0.7 \text{ s}^{-1}$ (from $\text{C}$-T$_1$), from NOESY spectrum at 325 K (maximum working temperature for THF). See, for example: J. Sandström, Dynamic NMR Spectroscopy, Academic Press, London, 1982, p. 96.


[19] In reference to the original double bonds in the neutral compound.

[20] Model calculations of the $D_{2h}$ symmetric dilithio ethylene group at the same level of theory for both the unsolvated and solvated forms (with $4H_2O$ ligands, $D_{2h}$) revealed an upfield shift of the sp$^2$ carbon atoms of as much as 45.6 ppm.

[21] $\text{C}_2$ symmetry would give rise to 16 proton and 28 carbon resonances.


[24] The picotube also undergoes reduction with a potassium metal compound.