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Controlled Spacing of 60-Carbon Spheres with 1,4-Cyclohexadienyl Ladders by Pairwise Diels−Alder Cycloaddition to Buckminsterfullerene

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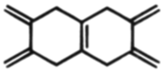
Buckminsterfullerene[1] differs from the other allotropes of carbon by being highly spherical and possessing unusual electronic,[2] magnetic,[3] and redox properties.[4] Although the C_{60} molecule is polyfunctional, its I_h symmetry can be disrupted in regiocontrolled fashion because of the significant reactivity differences inherent in its two types of carbon−carbon double bonds. Only those positioned between two six-membered rings become engaged in η^2 coordination to transition metals.[5] The somewhat longer 6:5 ring fusion double bonds likewise do not participate effectively in thermal [8 + 2],[6] [4 + 2],[7] [3 + 2],[8] [2 + 2],[9] and [2 + 1][10] cyclocondensations, or in photochemical additions.[11] As a consequence, isomerically pure monoadducts are relatively easy to isolate from such reaction mixtures. Many of these reactions are made possible because C_{60} is electron-poor[12] and has vacant orbitals at appropriate energy levels.[13]

Despite the facility with which C_{60} enters into these intermolecular reactions, little attention has been accorded to exploration of its derivatization with bifunctional dienes. In 1993, Müllen and co-workers reported that bis-*o*-quinodimethane does indeed capture two fullerene molecules to provide a bisadduct.[14] With our recent development of synthetic routes to **1−3**,[15] we have sought to explore the preparation of dumbbell-like systems (**4**) in which a pair of original C_{60} units are linked via 1,4-cyclohexadienyl ladders of different length. Since 1,4-cyclohexadiene rings can flex readily about an axis through their methylene carbon atoms,[16] the ladder in **4** is not rigid and substantial conformational folding is possible. Nevertheless, controlled spacing of the spheres in this manner is expected to greatly enhance our insight into the possible operation of intramolecular communication in the neutral hydrocarbons, their radical anions and polyanions, and selected alkali metal salts. The possibility of additional covalent linking between the fullerene units holds equal attraction, since these molecules would now resemble the [*n*]-beltenes[16−18] if cyclic, or buckyball pearl necklaces if polymeric.



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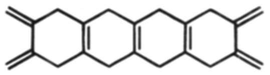

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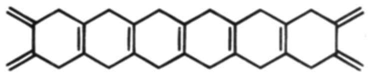

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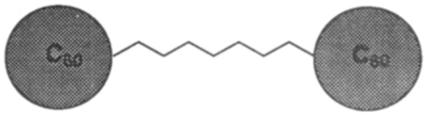

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Dropwise addition of **1** dissolved in toluene to a refluxing toluene solution containing 2 equiv of C_{60} resulted in the gradual appearance of an insoluble brown precipitate (**5**, 70%) during 8 h. This substance is completely insoluble in those solvents that commonly dissolve fullerenes. When **5** was heated in toluene at the reflux temperature for 24 h, the violet C_{60} color reappeared and the weight of residual solid decreased, suggesting that retro Diels−Alder reaction was occurring to some degree. The IR and Raman spectra of **5** indicated that the fullerene cages were intact. The structural features of **5** were ascertained by solid state ^{13}C NMR

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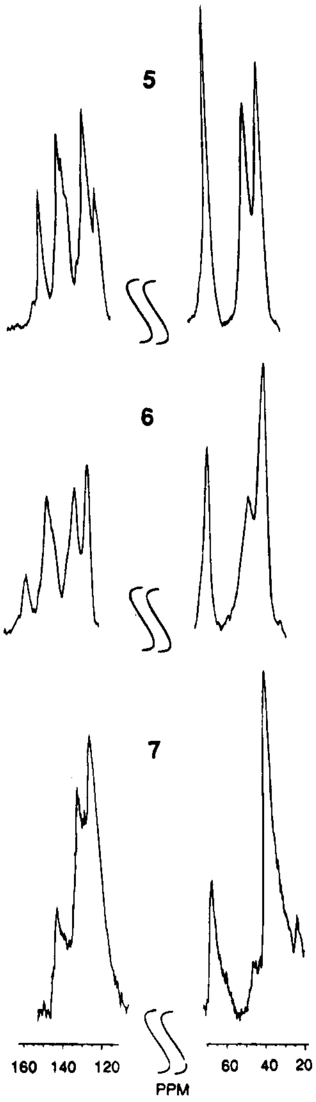


Figure 1. Solid state ^{13}C NMR analysis of **5**–**7** under TOSS-CPMAS conditions at 75 MHz. The measurements on **5** and **6** were performed on neat samples. In the case of **7**, an approximate 1:1 mixture with silica gel was utilized.

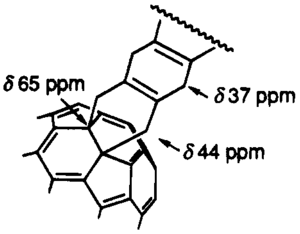
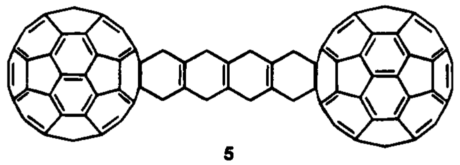


Figure 2. ^{13}C NMR assignment to **5**.

analysis using the total suppression of sidebands cross-polarization magic-angle spinning (TOSS CPMAS) experiment.[19] The appearance of multiple broad signals in the 120–170 ppm region (Figure 1) reflects the anticipated distortion within the fullerene sectors. The peak observed at 65 ppm is characteristic of those quaternary sp^3-hybridized carbons that constitute the point of attachment of the ladder (Figure 2).[7f] The pattern for the methylene carbons is as expected, with a modest upfield shift materializing as these centers become more distant from the deshielding cone surrounding the spheres. No mass spectral molecular ion was observed using FAB or laser desorption FT/ICR techniques in both positive- and negative-ion modes. The highest peak was seen at 720, possibly because of degradative fragmentation in the mass spectrometer. It is noteworthy, however, that thermal gravimetric analysis showed **5** to be stable to mass loss up to 415 °C in the solid state under argon.[20]

The termolecular condensations involving **2** and **3** with C_{60} were carried out in the predescribed manner to provide **6** (72%) and **7** (40%). These brown solids exhibited equally distinctive low solubility. In both cases, the TOSS CPMAS ^{13}C NMR spectrum corroborated the structural assignments (Figure 1). Attention is directed specifically to the fact that the relative intensity of the tetrahedral quaternary carbon signal at 65 ppm decreases progressively as the spacer length increases from 4 to 6 and ultimately to 8 units. Also, the ratio of the relative intensities of the 44 and 37 ppm absorptions, which approximates 1 in **5**, approaches 1:2 in **6**, and decreases still further in **7**. The IR and Raman spectra of **6** and **7** were very similar to that of **5**, and **6** was equivalently stable to mass loss up to 412 °C in the solid state under argon.



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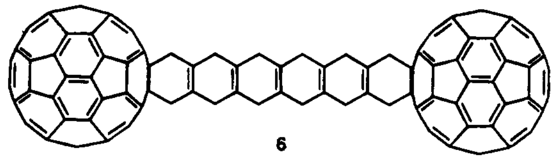

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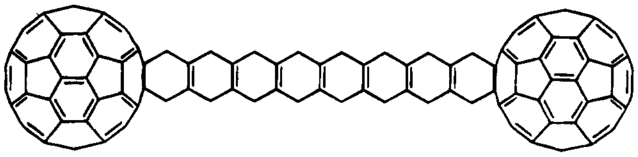

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In conclusion, the implementation of pairwise Diels–Alder reactions involving C_{60} and the multiply unsaturated bisdienes **1**–**3** gives rise to ladderlike structures having different extension levels. The 1,4-cyclohexadiene spacers have the ability to function as hinges because of the low-energy wide-amplitude bending modes available to them. Although the dumbbell-like structures described are very insoluble compounds, the very simple access route delineated here should prove applicable to other spatial arrangements where solubility would be less problematical. Further exploration along these lines can be expected to provide materials with promising properties and is being pursued.

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Supplementary Material Available: Experimental details (2 pages).

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