Aza-aziridinofullerene: Interconversion between Aza-aziridinofullerene and Bisazafulleroid

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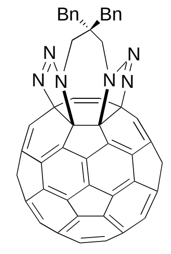
Abstract: The synthesis and spectroscopic characterization of a novel bisazafulleroid (**12**) and aza-aziridinofulleroid (**13**) are described. Treatment of C_{60} fullerene with the *C_2*-chiral bisazide **11** in refluxing chlorobenzene afforded bisazafulleroid **12** in 20% yield. When a solution of **12** was exposed to ambient light a quantitative conversion to the more polar **13**, in which the two imino groups add at both [5,6] and [6,6]-ring junctions, was observed. The two compounds exhibited characteristic absorption profiles in the electronic spectra and also showed distinct CD curves. Further, thermolysis of **13** in refluxing toluene resulted in a clean conversion to **12** within 10 min. ^{15}N-labeled **12** and **13** were synthesized to establish the structures. These observations provide the first example of an interconversion between an aza- and an aziridinofulleroid.

Keywords: azides · diastereoselectivity · fullerenes · interconversion

Introduction

Cycloaddition of organic azides to fullerene has been extensively investigated.[1–7] The nature of the azide appears to play a pivotal role on the selectivity of the reaction. In addition to monoadducts, it can add onto two [5,6]-ring junctions of an acenaphthene[3] or fluorene[4, 5] unit giving rise to regioisomers of bisazafulleroids. Alternatively, addition at the [6,6]-ring junctions of a phenanthrene unit has been observed[5, 6b] and the corresponding *N*-alkoxycarbonyl derivatives surprisingly yield the ring-opening adducts.[6] In our earlier report, we demonstrated[5] that the addition initially generates triazoline derivative **1**, which upon thermolysis gives aziridinofullerene **2** and/or azafulleroid **3** via dipolar or biradical intermediates. It is noteworthy that bisazafulleroids **3**–**5** are thermally stable and there is no interconversion between **2** and **3**.[4a,b] Recent reports from Mattay's group have shown the first photochemical rearrangement of an azafulleroid to aziridinofullerene.[2k] Triazolinofullerene derivative **6** gives aziridinofullerene **7** on photolysis, whereas thermolysis gives azafulleroid **8**. Irradiation of **8** at 300 nm gave **7** exclusively. Similar rearrangements have been shown to occur in the corresponding carbon analogues.[8] The pioneering works of Wudl, Diederich, and others[9] have shown that from the addition of carbene transfer reagents, such as diazo compounds to C_{60}, [5,6]-open fulleroids were obtained as the kinetic products, which underwent rearrangement to give the



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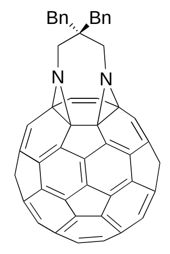

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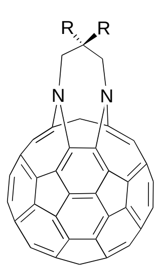
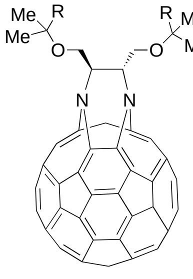


3 R = Bn

4 R = H



5a R = Me

5b R = Bn

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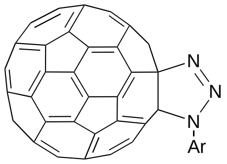

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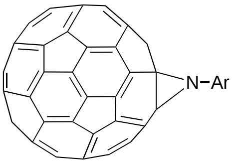

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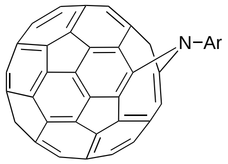

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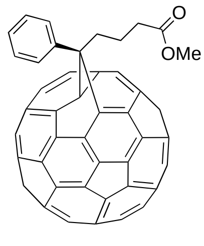

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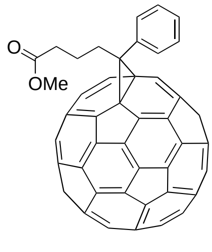

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thermodynamically stable [6,6]-closed methanofullerenes. Indeed this conversion was found to occur photochemically,[10] electrochemically,[11] and under acid catalysis.[12] Wudl proposed a di-π-methane rearrangement[10] in the photochemical conversion of the [5,6]-open fulleroid **9** to the [6,6]-closed methanofullerene **10**. This was supported by the observations of Shevlin[13] who demonstrated a photochemical step in the thermal rearrangement of a cyclopentylidene fulleroid to a methanofullerene. It is noteworthy that the rearrangement of methanofullerenes, or their imino analogues, back to the corresponding fulleroids has not been explored. In this paper we report the first example of an interconversion between a bisazafulleroid (**12**) and aza-aziridinofulleroid (**13**).

Results and Discussion

Bisazide **11**, obtained from 2,3-*O*-isopropylidene-L-threitol, afforded **12** in 20 % yield as a blackish brown solid, on treatment with C_{60} in refluxing chlorobenzene for 15 h, followed by a rapid workup and flash column chromatography on silica gel. The FAB-MS showed an $[M+1]$ peak at $m/z = 877.5$. In the ^{13}C NMR spectrum (Figure 1a), the C_1 symmetry is reflected by the 57 signals in the region δ 156–130, including three signals with an intensity of 2, in addition to the seven absorptions due to the tethering chain. The UV/visible spectrum of **12** (Figure 2) was found to be almost identical to that of the bisazafulleroid **4**,[4] in which the addition occurs at the two [5,6]-ring junctions of a fluorene unit.

^{13}C NMR investigations on ^{15}N-labeled (50 %) **12** clearly established the structure. Two sets of doublet of doublets at $\delta = 155.99$ ($J_{C-N} = 10.4$, 4.1 Hz) and 137.72 ($J_{C-N} = 6.6$, 2.4 Hz) were observed. These signals along with two doublets at $\delta = 136.27$ ($J_{C-N} = 13.4$ Hz) and 138.75 ($J_{C-N} = 5.0$ Hz) can be readily assigned to those carbons of the fullerene core connected to the two nitrogen atoms. The large coupling constant observed at $\delta = 136.27$ implies that the orientation of the lone pair of electrons on nitrogen atoms may contribute to this interaction.[14] Four additional doublets at $\delta = 137.80$, 135.69, 134.41, 132.98 along with a broad line at $\delta = 130.04$ due to long-range coupling were also observed. The two tertiary carbons at $\delta = 81.52$ and 78.37 resolved into a doublet. The two methylene carbons attached to two nitrogen atoms were observed as doublets with large coupling constants. An important feature of this ^{13}C NMR spectrum is the relatively downfield signal at $\delta = 155.99$. For the ^{15}N-labeled compound, unlike the signal at $\delta = 137.72$ that showed the expected splitting pattern, this

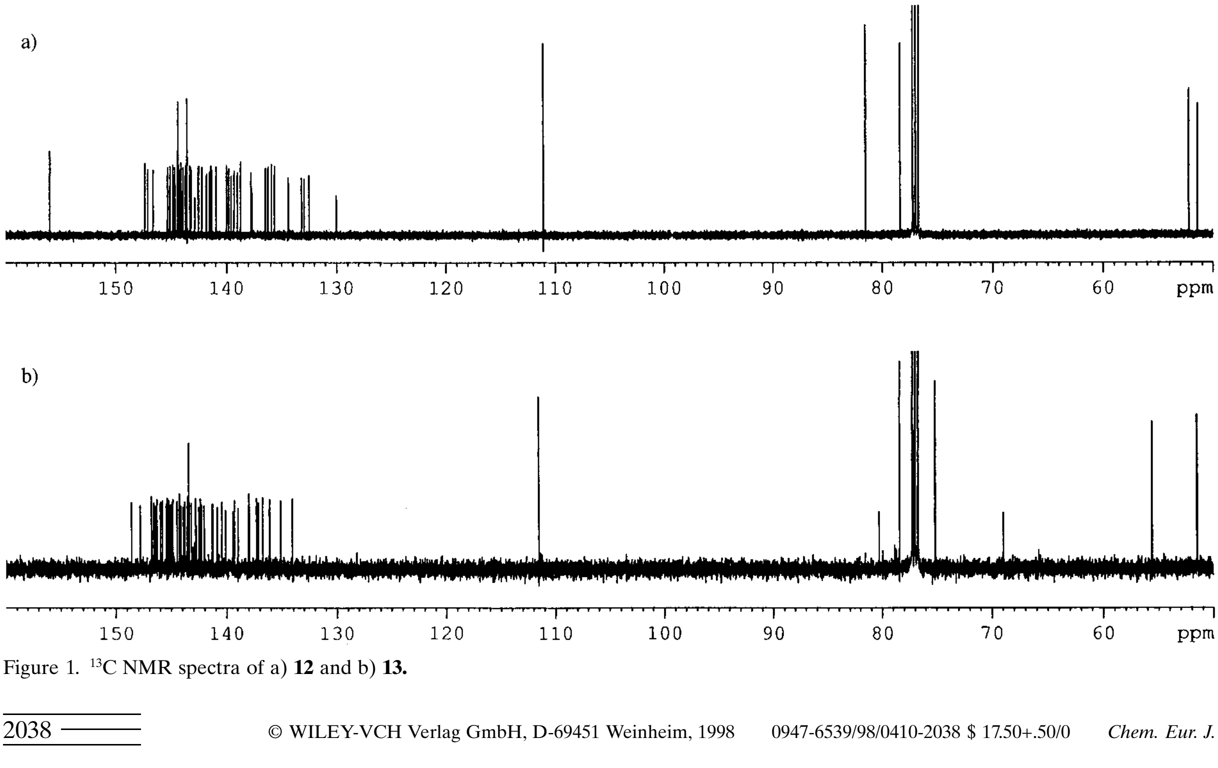


Figure 1. ^{13}C NMR spectra of a) **12** and b) **13**.

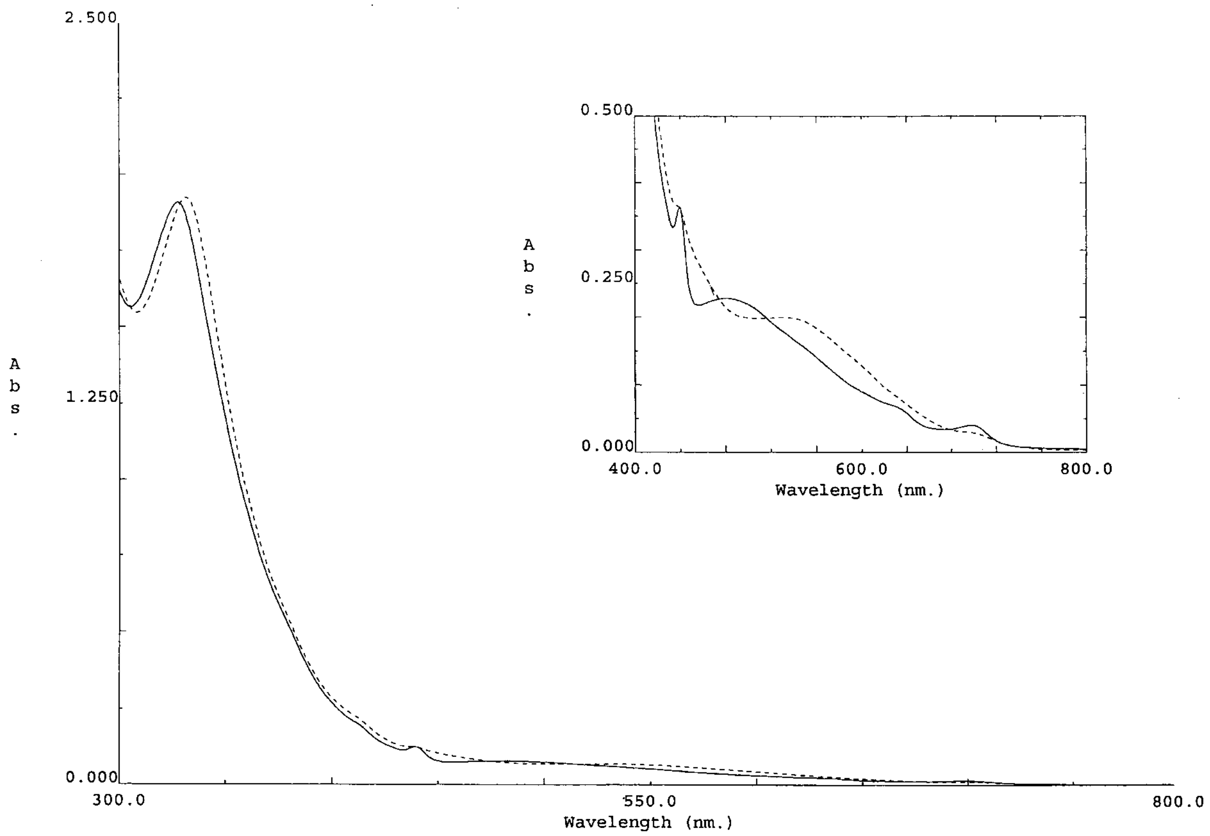


Figure 2. UV/Vis spectra for **12** (dotted line) and **13** (solid line) in toluene ($c = 4 \times 10^{-5}$ M; inset: $c = 1.2 \times 10^{-4}$ M).

signal at $\delta = 155.99$ resolved into five lines with a relative intensity of roughly 3:7:2:3:1. This indicates that there is significant isotopic shift, so that some of the absorptions come very close and appear as broad lines. From all these observations we infer that the tethering moiety is rigid and therefore it may be strained. This is also reflected in the ^{1}H NMR spectrum of **12** in which two of the methylene protons appeared at comparatively low field, one as doublet of doublets at $\delta = 4.38$ and the other around $\delta = 4.7$ overlapped with other signals.

Compound **12** is stable in the dark. However, when a solution of **12** in chlorobenzene, toluene, toluene/hexane mixture, chloroform, or dichloromethane was exposed to ambient light, a quantitative conversion to the more polar **13** was observed. The electronic absorption spectrum showed significant difference in the visible region with characteristic absorptions at 439 and 698 nm indicative of a [6,6]-closed adduct (Figure 2). Further, the two compounds exhibited distinct circular dichroism (CD) curves (Figure 3). In the ^{1}H NMR spectrum, the two sets of methyl protons appeared as two sharp singlets at $\delta = 1.62$ and 1.65. The remaining six protons appeared in the region $\delta = 3.86–5.08$ and exhibited a totally different spectral pattern compared with **12**. In the ^{13}C NMR spectrum of **13** (Figure 1b), the two sp^3 carbons corresponding

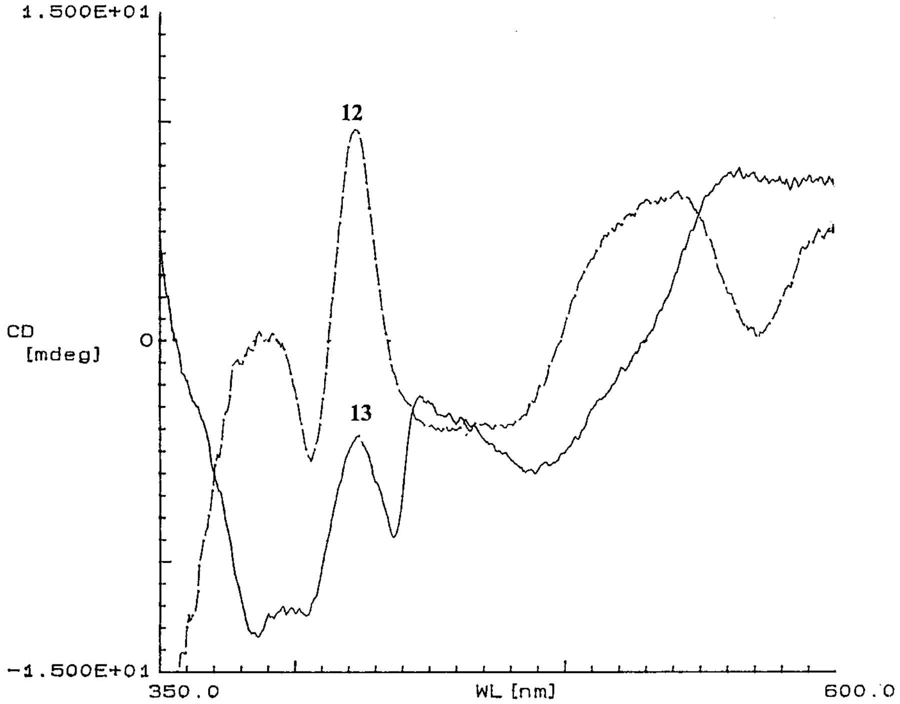
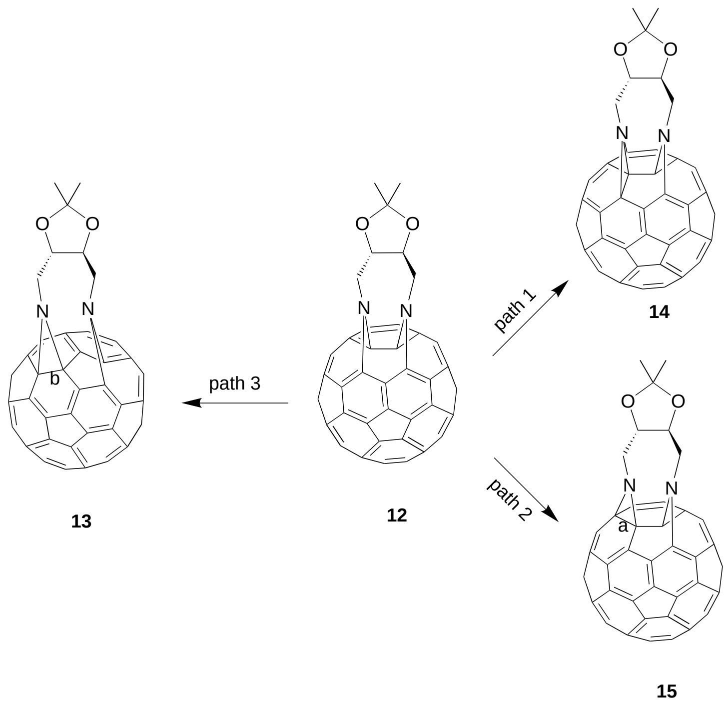


Figure 3. CD curves for **12** and **13** in toluene ($c = 4 \times 10^{-5}$ M).

to the fullerene core appeared at $\delta = 69.0$ and 80.30, in addition to signals due to other sp^3 carbons. The remaining fullerene carbons appeared as 57 lines with one having an intensity of 2. Apparently, one of the imino groups in **12** undergoes ring closure at one of the ring junctions resulting in the formation of an aza-aziridinofulleroid. Three possible structures can arise as a result of this ring closure (Scheme 1). One is a direct [5,6]-ring closure to give [5,6]-open-[5,6]-closed **14** (path 1). Secondly, [5,6]-ring closure followed by a 1,5-sigmatropic shift in a similar manner to that found in the di-π-methane rearrangement[10] to form the [5,6]-open-[6,6]-closed fulleroid. In this case there are two possibilities. The nitrogen can migrate to either position *a* to give **15** (Scheme 1, path 2) or position *b* leading to **13** (path 3). In order to differentiate between these possibilities, the ^{13}C NMR of the ^{15}N-labeled **13** was investigated. The methylene carbon at $\delta = 51.50$ split into a doublet of doublets and that at $\delta = 55.59$ into a doublet. It is interesting to note that one of the methine carbons exhibited long-range coupling with both nitrogen atoms, whereas the other one showed only broadening. Five additional doublets were observed at $\delta = 134.08$ ($J_{\text{C-N}} = 5.3$ Hz), 137.99 ($J_{\text{C-N}} = 6.0$ Hz), 139.45 ($J_{\text{C-N}} = 7.0$ Hz), 142.06 ($J_{\text{C-N}} = 2.6$ Hz), and 148.65 ($J_{\text{C-N}} = 5.3$ Hz). It is important to note that none of these fullerene carbon absorptions, other than the one at $\delta = 69.0$ that corresponds to one of the sp^3 carbons, appeared as doublet of doublets, whereas a minimum of two absorptions involving both ^1J and ^2J couplings might be expected for structures **14** and **15**. Accordingly, these structures were ruled out. Hence the migration may follow path 3 giving compound **13**. We were not surprised to see that the aziridine carbon at $\delta = 69.0$ exhibited long-range coupling, an indication of the close proximity of the second nitrogen atom.[15] Since the splitting pattern and coupling constants of this carbon are comparable to those of the signal at $\delta = 155.99$ of the bisazafulleroid, it appears that these carbons exhibit isotopic shifts to the same extent.



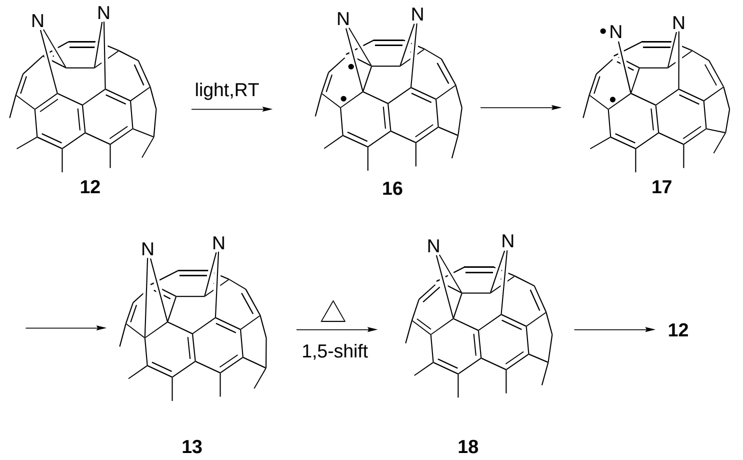
Scheme 1. Possible pathways for the rearrangement of **12**.

Thermolysis of **13** in refluxing toluene resulted in a clean conversion to **12** within 10 min [Eq. (1)]. It should be mentioned that **12** was also obtained by heating a solid sample of **13** at 100 °C for 1 h. ^{1}H NMR, UV-Vis

$$\mathbf{12} \xrightleftharpoons[110\,^{\circ}\mathrm{C}]{\text{light, RT}} \mathbf{13} \tag{1}$$

spectroscopy or CD experiments can be used for monitoring the interconversion. In our experiments we found that, in the conversion of **12** to **13**, a solution of **12** in CDCl$_3$ in an NMR tube, when protected from ambient light showed no change in the spectral pattern even after two weeks. However, when this solution was exposed to ambient light a clean conversion occurred. So it is evident that, as in the case of methanofullerenes, a photochemical rearrangement is taking place. The driving force may be the strain associated with the tethering chain, so that migration occurs even in ambient light. It was observed that the thermal conversion of the aziridine to the aza derivative proceeds even in the dark. The thermal rearrangement of annelated azepines has been reported.[16] So it is anticipated that under thermal activation a 1,5-sigmatropic shift takes place to give intermediate **18**, which can then undergo a disrotatory ring opening to regenerate the azafulleroid **12** (Scheme 2).

It is worth noting that the conversion of **12** to **13** is highly stereoselective. In the NMR spectrum of **12**, two of the methylene protons and one carbon atom showed unusual downfield shift. Accordingly, it is likely that this strained imino moiety preferably undergoes rearrangement to afford **13.** However, in the case of **13**, spectral evidence indicates that the strain is not completely relieved and possibly under thermal activation this group again



Scheme 2. Possible mechanism for the interconversion between **12** and **13** (substituent on nitrogen omitted for clarity).

migrates back to regenerate **12**. In other words, the strain in **12** and **13** serves as the driving force for this back and forth migration of the imino group on the surface of C_{60}, and this rearrangement is highly diastereoselective. The NMR assignments very clearly demonstrate this facial selectivity in the migration. This reversible rearrangement under very mild conditions is of special synthetic interest especially when regio- and stereoselective additions to C_{60} are very difficult. The transfer of chiroptical properties from addends to the fullerene core is well documented.[17] Our results suggest that desymmetrization of C_{60} by means of a chiral addend may influence the diastereoselectivity in further reactions onto the fullerene skeleton.

Experimental Section

1,4-diazido-1,4-dideoxy-2,3-*O*-isopropylidene-L-threitol (11): A solution containing 1,4-di-*O*-methanesulfonyl-2,3-*O*-isopropylidene-L-threitol (1.1 g, 3.45 mmol) and sodium azide (898 mg, 13.8 mmol) in dry DMF (50 mL) was stirred at 80–90 °C for 20 h. The solvent was removed under reduced pressure. The residue was diluted with water (50 mL) and extracted with ether (3 × 20 mL). The organic layer was washed with brine, dried ($MgSO_4$), and evaporated in vacuo to give **11** as a pale yellow liquid (590 mg, 80%), which was used in the next step without further purification. ^1H NMR ($CDCl_3$, 200 MHz): $\delta = 4.03$ (m, 2H), 3.53 (m, 2H), 3.30 (m, 2H), 1.44 (s, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 110.04$, 76.61, 51.22, 26.52. IR (neat): $\tilde{\nu} = 2110$, 1384, 1376 cm^{-1}.

Bisazafulleroid 12: A solution of the bisazide **11** (138 mg, 0.65 mmol) in chlorobenzene (100 mL) was added to a refluxing solution of C_{60} (360 mg, 0.5 mmol) in chlorobenzene (260 mL, deoxygenated) during a period of 45 min under a nitrogen atmosphere. After the addition, the reaction mixture was refluxed for 15 h. The solvent was removed under reduced pressure, and the residue was subjected to flash column chromatography on silica gel. Elution with hexane/toluene (20:1) gave 100 mg (28%) of unreacted C_{60}. Further elution (hexane/toluene 4:1)[18] afforded **12** as a black-brown solid (65 mg, 20% based on reacted C_{60}). ^1H NMR ($CS_2/CDCl_3$, 500 MHz): $\delta = 4.77–4.65$ (m, 3H), 4.38 (dd, $J = 10.6$, 1.3 Hz, 1H), 3.84 (dd, $J = 13.0$, 5.8 Hz, 1H), 3.68 (dd, $J = 13.0$, 10.0 Hz, 1H), 1.63 (s, 3H), 1.61 (s, 3H); ^{13}C NMR ($CS_2/CDCl_3$, 125 MHz): $\delta = 155.99$ (dd, $J_{C-N} =$ 10.4, 4.1 Hz), 147.42, 147.40, 147.13, 146.66, 145.35, 145.15, 144.88, 144.73, 144.71, 144.49, 144.44, 144.43 (2C), 144.40, 144.34, 144.24, 144.20, 144.18, 144.17, 144.00, 143.78, 143.74, 143.68, 143.62 (2C), 143.61 (2C), 143.36, 143.34, 143.32, 143.23, 142.89, 142.60, 142.57, 142.26, 141.86, 141.61, 141.58, 141.49, 141.34, 141.00 (d, $J_{C-N} = 1.6$ Hz), 140.03, 139.82, 139.62, 139.36, 139.06, 138.75 (d, $J_{C-N} = 5.0$ Hz), 137.80 (d, $J_{C-N} = 3.5$ Hz), 137.72 (dd, $J_{C-N} = 6.6$, 2.4 Hz), 136.52, 136.27 (d, $J_{C-N} = 13.4$ Hz), 135.96, 135.69 (d, $J_{C-N} = 3.6$ Hz), 135.66, 134.41 (d, $J_{C-N} = 1.9$ Hz), 133.23, 132.98 (d, $J_{C-N} =$ 2.1 Hz), 132.53, 130.04 (broad), 111.10, 81.52 (d, $J_{C-N} = 3.9$ Hz), 78.37 (d, $J_{C-N} = 2.1$ Hz), 52.22 (d, $J_{C-N} = 7.5$ Hz), 51.45 (d, $J_{C-N} = 12.9$ Hz), 26.87, 26.82; FAB-MS (NBA): *m/z*: 877.5 [$M^+ + 1$].

Aza-aziridinofulleroid 13: A solution of the bisazafulleroid **12** (65 mg) in CH_2Cl_2 (600 mL; a few drops of CS_2 were added to ensure solubility) was kept exposed to ambient light. After 4 h TLC showed complete conversion to **13**. Solvent was removed in vacuo at room temperature to give **13** as a brown solid. ^1H NMR ($CS_2/CDCl_3$, 500 MHz): $\delta = 5.07$ (dd, $J = 10.0$, 5.7 Hz, 1H), 4.95 (ddd, $J = 10.0$, 8.8, 5.7 Hz, 1H), 4.83 (dt, $J = 8.8$, 2.8 Hz, 1H), 4.50 (dd, $J = 13.4$, 8.8 Hz, 1H), 4.44 (dd, $J = 13.4$, 2.8 Hz, 1H), 3.88 (t, $J = 10.0$ Hz, 1H), 1.65 (s, 3H), 1.62 (s, 3H); ^{13}C NMR ($CS_2/CDCl_3$, 125 MHz): $\delta = 148.65$ (d, $J_{C-N} = 5.3$ Hz), 147.84, 146.84, 146.64, 146.62, 146.61, 146.45, 146.31, 146.01, 145.83, 145.52, 145.43, 145.42, 145.29, 145.27, 145.14, 145.11, 144.95, 144.94, 144.54, 144.34, 144.30, 144.29, 144.18, 143.95, 143.84, 143.61, 143.56, 143.45 (2C), 143.41, 143.24, 143.23, 142.85, 142.81, 142.55, 142.42, 142.40, 142.30, 142.06 (d, $J_{C-N} = 2.6$ Hz), 141.38, 141.35, 141.29, 140.90, 140.49, 140.13, 139.45 (d, $J_{C-N} = 7.0$ Hz), 139.33, 139.00, 138.06, 138.00, 137.99 (d, $J_{C-N} = 6.0$ Hz), 137.35, 137.17, 136.78, 136.16, 135.14, 134.08 (d, $J_{C-N} = 5.3$ Hz), 111.57, 80.30 (d, $J_{C-N} = 9.2$ Hz), 78.40 (brs), 75.16 (dd, $J_{C-N} = 3.5$, 1.8 Hz), 69.0 (dd, $J_{C-N} = 10.1$, 4.1 Hz), 55.59 (d, $J_{C-N} =$ 3.9 Hz), 51.50 (dd, $J_{C-N} = 7.9$, 3.2 Hz), 27.08, 26.99; FAB-MS (NBA): *m/z*: 877.5 [$M^+ + 1$].

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