Unprecedented ring expansion of [60]fullerene: incorporation of nitrogen at an open 6,6-ring juncture by regiospecific reduction of oxycarbonylaziridino-[2′,3′ : 1,2][60]fullerenes. Synthesis of 1a-aza-1(6a)-homo[60]fullerene, $C_{60}H_2NH$

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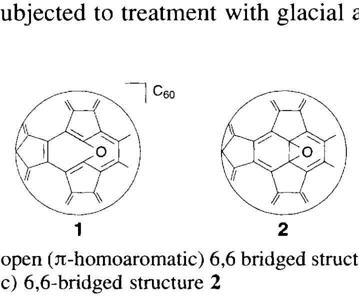
Upon treatment with zinc in glacial acetic acid, *N*-oxycarbonylaziridino[2′,3′ : 1,2][60]fullerenes 3 undergo a reversible reductive cleavage of the bridgehead C–C bond to provide the first examples of bridged fulleroids 4 having an open 6,6-ring juncture; deprotection of the *N-tert*-butoxycarbonyl derivative 4a allows the convenient synthesis of $C_{60}H_2NH$ 5, the parent member of this new class of bridged fulleroids.

A key aspect of fullerene chemistry is the nature of bonding in isolable mono-adducts, *e.g.* $C_{60}O$.[1] In this context, classical studies of the parent oxidoannulene, *cf.* **1** and related species by Vogel[2] suggest that $C_{60}O$ should possess an open (π-homoaromatic) 6,6-bridged fulleroid structure **1** (Fig. 1), but experimental evidence based on ^{13}C NMR data has proved conclusively that the structure is closed (σ-homoaromatic) **2**.[1] Likewise, other known 6,6-bridged mono-adducts *e.g.* $C_{61}H_2$,[3] $C_{60}NH$,[4] and others,[5] have been shown to possess σ-homoaromatic structures, and this structural preference can be explained by the need to maintain, as closely as possible, the bonding situation found in [60]fullerene itself, *i.e.* double bonds radiating away from pentagons, *cf.* thermodynamically disfavoured open 6,6-bridged structure **1** that requires two double bonds at the bridgehead as well as three double bonds in pentagons.[6] In continuation of our studies into the structural modification of the fullerene core,[7–9] we have now succeeded in preparing the first examples of open 6,6-bridged compounds by the simple expedient of selectively reducing the bridgehead C–C bond of closed 6,6-bridged aziridinofullerenes **3** to give the dihydro derivatives **4** having a bridged ten-membered ring. We also report here the preparation and structural characterisation of the parent compound $C_{60}H_2NH$ **5** by deprotection of *N-tert*-butoxycarbonyl derivative **4a**. In sharp contrast to the known lability of hydrogenated fullerene derivatives, *e.g.*$C_{60}H_2$, especially towards aerial oxidation,[10] the isolated product **5** is remarkably air-stable and easily handled, although under basic conditions undergoes an unusual oxidative ring contraction to aziridinofullerene **6**.

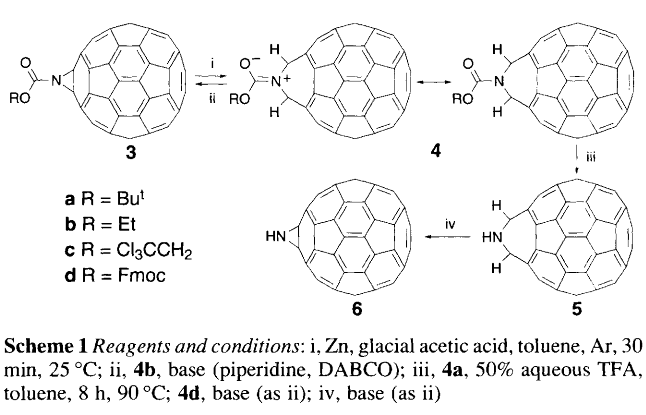
Thus, when a mixture of *N-tert*-butoxycarbonylaziridino-[2′,3′ : 1,2][60]fullerene **3a**[4] (1 equiv.) and zinc (300 equiv.) in toluene was subjected to treatment with glacial acetic acid (10 equiv.), after 30 min the dihydrofulleroid derivative **4a** was obtained in virtually quantitative yield and readily purified by flash chromatography (hexane–toluene, silica) (Scheme 1). FAB–MS analysis of product **4a** [$(M^+ + 1)$ 838.08750, $C_{65}H_{12}NO_2$ requires 838.08680] confirmed that the aziridinofullerene **3a** [molecular mass 835] had undergone reduction with the incorporation of two hydrogen atoms.



1 **2**

Fig. 1 Proposed open (π-homoaromatic) 6,6 bridged structure **1**, and closed (σ-homoaromatic) 6,6-bridged structure **2**

Evidence for addition of the two hydrogens symmetrically across the aziridine moiety in **3a** with ring expansion to **4a** was provided by comparison of ^{13}C NMR data. The spectrum of **4a**[†] was essentially the same as that for the aziridinofullerene **3a**, particularly in the sp^2 region of the spectrum, thus showing that the product had retained C_{2v} symmetry (17 lines, 16 of which are in the sp^2 region). In the diagnostic sp^3 region of the spectrum, the carbon atoms bonded directly to nitrogen in **3a** (δ 81.0) had been replaced with two broad signals at δ 61.8 and 62.9. This non-equivalence arising from rupture of the 1,2-C–C fullerene bond is indicative of restricted rotation about the N–CO amide bond in **4a**[‡] and is further reflected in the ^1H NMR spectrum by the appearance of two broad singlets for the hydrogens, albeit at the unusually high values of δ 9.10 and 9.35 due to the strong deshielding effect arising from the close proximity to pentagonal rings.[11] On cooling to −60 °C, the broad singlets became two well resolved doublets ($^4J_{H-H}$ = 3.64 Hz) owing to coupling along the 'W' path.[12] Additional evidence for restricted rotation was found in the shift observed for the carbonyl group in the FT-IR spectrum of **4a** (1705 *vs.* 1738 cm^{-1} for **3a**). Interestingly, the UV-VIS spectrum of a faintly pink solution of **4a** in hexane displayed typical absorptions due to the fullerene skeleton at λ_{max} at 256.5 nm (ε/dm^3 mol^{-1} cm^{-1} 1.90×10^4) and 315.5 (5.95×10^3) as well as the weak, but characteristically significant sharp feature at 432 (5.20×10^2), which is usually indicative of bridging about a closed 6,6-ring junction.[3]



Scheme 1 *Reagents and conditions*: i, Zn, glacial acetic acid, toluene, Ar, 30 min, 25 °C; ii, **4b**, base (piperidine, DABCO); iii, **4a**, 50% aqueous TFA, toluene, 8 h, 90 °C; **4d**, base (as ii); iv, base (as ii)

For preparation of the parent compound $C_{60}H_2NH$ **5**, the *tert*-butoxycarbonyl protecting group in **4a** is cleaved under acidic conditions (Scheme 1). The reaction was completed upon heating for 8 h at 90 °C in 50% aqueous trifluoroacetic acid (TFA)–toluene to give **5** (90%), which is purified by precipitation from CS_2 by addition of acetone, followed by washing with pentane [FAB–MS (M^+) 737.02558, $C_{60}H_3N$ requires 737.02655]. The unique structure of **5**§ was confirmed by ^1H and ^{13}C NMR spectroscopy, both of which showed much less complexity now that the element (*tert*-butoxycarbonyl group) responsible for the restricted rotation phenomenon (*vide supra*) had been eliminated. Thus, in place of the signals at δ 61.8 and 62.9 in the ^{13}C NMR spectrum of **4a** appeared a singlet at δ 65.9, whilst the corresponding resonances in the ^1H NMR spectrum (600 MHz) were replaced by a sharp singlet at *ca.* δ 7.7, which by inverse detection[13] showed a one bond C–H coupling constant ($^1J_{C\text{–}H}$ = 137.6 Hz) typical for such sp^3 protons.[14] The only other signals in the ^{13}C NMR spectrum of **5** were 16 lines between δ 135.37 and 152.95, which is fully consistent with C_{2v} symmetry. The UV–VIS spectrum of the faintly yellow solution of **5** in TCE exhibited a weak but significant sharp feature at 433 nm (ε/dm^3 mol^{-1} cm^{-1} 1.45×10^3) as well as the characteristic fullerene band at 315 (1.47×10^4).

The site specific reduction of **3a** to **4a** appears to be a general reaction of *N*-oxycarbonylaziridinofullerenes¶ and occurred readily with derivatives **3b–d**[15] (>90%). In each case, the dihydrofulleroids **4b–d** exhibited the same ^{13}C and ^1H NMR, FT-IR and UV–VIS spectral features as **4a**. Our attempts to deprotect **4c** under the same conditions as an alternative method of preparing **5** failed. However, treatment of a toluene solution of **4d** with either piperidine, 1,4-diazabicyclo[2.2.2]octane (DABCO) or neutral alumina, caused elimination of the Fmoc group to produce **5** as shown by HPLC analysis [FullereneSep[16] (25 × 0.46 cm column, hexane–ethyl acetate (85 : 15), F_R = 2.0 ml min^{-1}, 258 nm)], but the compound proved to be unstable under the basic conditions employed, and within minutes underwent oxidative ring closure to $C_{60}NH$ **6**. Further investigation into this unexpected ring contraction has shown the reaction to be irreversible, although when the dihydrofulleroid derivative **4b** is subjected to piperidine or neutral alumina, closed aziridinofullerene **3b** can be regenerated quantitatively, thus demonstrating for the first time the feasibility of controlled ring opening–closing reactions of the fullerene cage. Cyclic voltammetry (CV) of **3b** under argon‖ shows a set of redox peaks (reduction peak at *ca* −700 mV, oxidation peak at *ca.* −550 mV), which we attribute to the one electron reduction of the fullerene cage. Continued cycling to more negative potentials, results in further reduction and the progressive growth of a second set of redox peaks (reduction peak at *ca.* −820 mV, oxidation peak at *ca.* −670 mV), both of which occur at similar potential to the redox peaks seen for drop-coated [60]fullerene (reduction at *ca.* −860 mV, oxidation at *ca.* −670 mV); this illustrates that the closed ring decreases the first reduction potential with respect to [60]fullerene, but further reduction leads to a chemical reaction at the closed ring and the loss of this effect. Similar studies of drop-coated dihydrofulleroid **4b** show no electroactivity in this region, with the reduction being shifted to a more negative potential, thus demonstrating that an open 6,6-ring juncture inhibits electrochemical reduction of the fullerene skeleton.

Footnotes

† **4a**: ^1H NMR (200 MHz, CS_2–$CDCl_3$) δ 1.91 (9 H, s, Bu^t), 9.10 (1 H, bs, CHNC*H*), 9.35 (1 H, bs, C*H* NCH); ^{13}C NMR (62.5 MHz, CS_2–$CDCl_3$) δ 154.6, 149.6 (C=O), 148.6, 147.5, 146.6, 145.6, 145.4, 144.9, 143.8, 143.1, 142.9, 142.8, 142.4, 139.5, 138.6, 138.1, 133.9 (br.), 83.3 (Bu^t–O–), 62.9 (br., H*C*NCH), 61.8 (br., HCN*C*H), 28.1 (Bu^t); ν_{max} (KBr)/cm^{-1} 2918 (C–H), 1705 (C=O), 523 (fullerene).

‡ Observation of a sp^3 carbon signal at *ca.* δ 62 discounts the alternative site of hydrogen addition in which C_{2v} symmetry is maintained, *viz.* at the opposite pole of the fullerene sphere for which one would expect to see two sp^3 carbon signals between δ 50–80 (C–N and C–H), and consequently only 15 lines in the sp^2 region. Restricted rotation about the amide N–CO bond in such a molecule would not be manifested.

§ **5**: ^1H NMR (250 MHz, CS_2–$^2[H]_6$benzene) δ 7.57; (CS_2–$CDCl_3$) δ 7.75; (CS_2–CD_2Cl_2) δ 7.81; (CS_2-$^2[H]_6$acetone) δ 7.82; ^{13}C NMR (62.5 MHz, CS_2–$^2[H]_6$benzene) δ 152.9 (4C), 149.3 (2C), 148.4 (2C), 148.2 (4C), 147.2 (4C), 146.0 (4C), 145.4 (4C), 144.5 (4C), 143.8 (4C), 143.5 (4C), 143.4 (4C), 142.9 (2C), 140.1 (4C), 139.4 (4C), 138.6 (4C), 135.3 (4C), 65.9 (2C, H*C*N*C*H); ν_{max} KBr)/cm^{-1} 3400 (N–H), 2921 (C–H), 524.3 (fullerene).

¶ The reductive procedure does not appear to be extendible to methanofullerenes (ref. 6); the carbon analogue of **3b** was inert to the same reaction conditions.

‖ Carried out by drop-coating a sample in CH_2Cl_2 onto a platinum electrode and recording the CV in MeCN–0.1 mol dm^{-3} $LiClO_4$ with respect to Ag/Ag^+ (0.01 mol dm^{-3}).

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