

## Aziridino[2',3':1,2][60]fullerene

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Studies into the chemical reactivity of fullerenes, particularly [60]fullerene have grown rapidly in the past two years following the isolation of C<sub>60</sub>O and its identification as an epoxide which is formed across the 6,6-central bond of a pyracyclene unit.<sup>1,2</sup> Chemically, the oxygen is not firmly bound and like many other derivatives, C<sub>60</sub>O shows a tendency to revert to [60]fullerene upon heating (toluene, 110 °C, 24 h).<sup>2</sup> We now report the preparation of the nitrogen analogue, C<sub>60</sub>NH<sup>+</sup> **1**, which in sharp contrast to C<sub>60</sub>O, is a thermally stable derivative which can be heated to 147 °C (1,1,2,2-tetrachloroethane, TCE) without change. Thus, the synthesis of bronze-coloured **1** is conveniently achieved by a two-step process as outlined in Scheme 1.

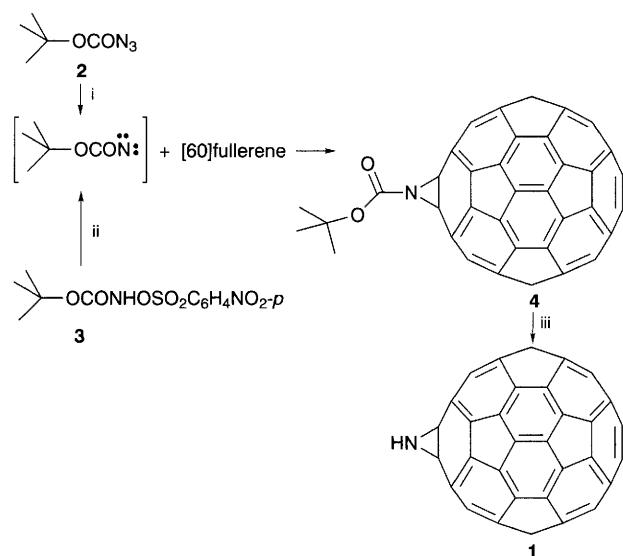
The first step involved dropwise addition to a solution of [60]fullerene in boiling TCE of *tert*-butylazidoformate **2**,<sup>3</sup> which is stored as a 3 mol dm<sup>-3</sup> stock solution in TCE thus minimising the intrinsic danger of azides.<sup>4</sup> The outcome was elimination of nitrogen, and within minutes, the formation of *N*-*tert*-butoxycarbonylaziridino[2',3':1,2][60]fullerene **4**,<sup>‡</sup> by *in situ* trapping of the intermediate nitrene (Bu<sup>+</sup>O<sub>2</sub>CN:) with [60]fullerene.<sup>5</sup> The same result could also be achieved, albeit under much milder conditions, by base-induced α-elimination<sup>6</sup> of *O*-4-nitrophenylsulfonyl-*tert*-butylhydroxamic acid **3**<sup>§</sup> in the presence of [60]fullerene under phase-transfer conditions at room temperature.<sup>7</sup> By both these procedures, compound **4** is obtained in 55–60% yield, and is easily purified by flash chromatography on silica (*n*-hexane–toluene).

In the second step, compound **4** was heated in TCE (5 h), whence elimination of isobutene and CO<sub>2</sub> occurred to form the title compound **1** in 70% yield. No evidence was found for a fullerenoaziridine-oxazole (or aziridinofullerene-oxazolo-

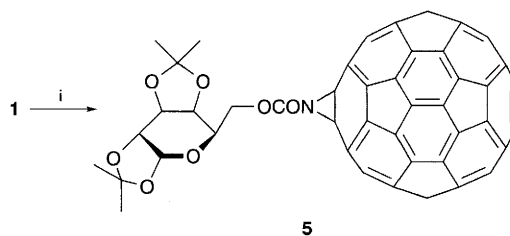
fullerene) rearrangement previously observed for this class of compounds.<sup>4,5,6</sup> Pertinently, no molecular ion at 835 (C<sub>65</sub>H<sub>9</sub>NO<sub>2</sub> requires 835) was observed in the FAB mass spectrum of **4**, but ions at 780.00969 [(M<sup>+</sup> + 1), C<sub>61</sub>H<sub>2</sub>NO<sub>2</sub> requires 780.00855] and 736.01497 [(M<sup>+</sup> + 1), C<sub>60</sub>H<sub>2</sub>N requires 736.01872] were measured and correspond to the sequential loss of isobutene and CO<sub>2</sub> from **4**.

The structural assignment of **1** rests on spectroscopic arguments and attempts are being made to produce a highly crystalline derivative of **1** for X-ray crystallographic analysis. FAB-MS analysis of **1** showed a prominent molecular ion at 736 [(M<sup>+</sup> + 1), 736.01199, C<sub>60</sub>NH<sub>2</sub> requires 736.01872]. The <sup>13</sup>C NMR spectrum is consistent for a molecule with C<sub>2v</sub> symmetry incorporating an aziridine ring at a 6,6-junction of [60]fullerene with fast pyramidal inversion at nitrogen.<sup>8</sup> Hence, there are 16 lines in the fullerene region δ 147 and 138 (13 lines of intensity 4, 3 lines of intensity 2) and a diagnostically significant peak in the sp<sup>3</sup> region at δ 79.12 (CS<sub>2</sub>-[<sup>2</sup>H<sub>6</sub>]acetone) [δ 78.71 (CS<sub>2</sub>-CDCl<sub>3</sub>)]; lines owing to the carbonyl and *tert*-butyl carbon atoms in the precursor **4** were absent. Similarly, in the <sup>1</sup>H NMR spectrum of **1** the resonance at δ 1.7 owing to the *tert*-butyl group had disappeared and was replaced by a broad signal assignable to NH at δ 5.9, which disappeared on deuteration. In the FT-IR (KBr) spectrum of **1** there was no carbonyl band and the main bands were 3272 (w, NH), 1426.6, 1184.0, 1039.8, 706.3, 615.7, 566.7, 526.3 and 497.1 cm<sup>-1</sup>. It is noteworthy that four of these bands resemble the principal absorption of [60]fullerene (1429.0, 1182.7, 575.9, 526.9).<sup>1</sup> The UV-VIS spectrum of the faintly pink dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) solution of **1** displayed typical absorptions due to the fullerene skeleton at λ<sub>max</sub> 258.5 nm (ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 3.05 × 10<sup>4</sup>), and 326.5 (9.03 × 10<sup>3</sup>), together with a shoulder at 410.5 and a weak but sharp feature at 423.5 (1.94 × 10<sup>3</sup>). These data compare favourably with those reported for closed 6,6-compounds such as C<sub>60</sub>O<sup>1,2</sup> (1,2-epoxy[60]fullerene) and C<sub>61</sub>H<sub>2</sub><sup>9</sup> (1,2-methano[60]fullerene) and so it is concluded that the structure of **1** is that of a closed [6,6]-aziridinofullerene.

We are currently exploring the potential of **1** to undergo ring-opening reactions of strained aziridines, thus providing a valuable route to 1,2-addition products and their further elaboration. We are also investigating the functionalisation of **1**, and in this connection we wish to report the quantitative



**Scheme 1** Reagents and conditions: i, TCE, 147 °C; ii, NaHCO<sub>3</sub>, BzEt<sub>3</sub>NCl, H<sub>2</sub>O–TCE–CH<sub>2</sub>Cl<sub>2</sub>, 20 °C; iii, TCE, 147 °C, 5 h



**Scheme 2** Reagents and conditions: i, 1,2:3,4-di-*O*-isopropylidene-D-galactopyranose-6-chloroformate, pyridine, TCE, 22 °C, 2 h

formation of D-galactose derivative **5**¶ by direct acylation under mild conditions (Scheme 2).

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### Footnotes

† Herein we describe C<sub>60</sub>NH **1** as aziridino[2',3':1,2][60]fullerene on the basis of an IUPAC recommendation that in all compounds in which a heterocyclic ring is fused to a fullerene, the latter is to be the 'root' compound and will take priority in numbering, but we note that an alternative name (also IUPAC recommended) is 1,2-epimino-[60]fullerene.

‡ Selected data for **4**: <sup>1</sup>H NMR (250 MHz, CS<sub>2</sub>-CDCl<sub>3</sub>) δ 1.7 (s, 9H, Bu<sup>t</sup>); <sup>13</sup>C NMR (62.5 MHz, CDCl<sub>3</sub>) δ 154.4 (C=O), 144.9 (4C), 144.8 (4C), 144.5 (4C), 144.3 (2C), 144.2 (4C), 143.7 (4C), 143.4 (2C), 142.8 (8C), 142.7 (8C), 142.5 (2C), 141.9 (4C), 141.8 (4C), 140.7 (4C), 139.6 (4C), 83.3 (2C), 29.7 (quat. C), 27.6 (Bu<sup>t</sup>); FT-IR ν<sub>max</sub>/cm<sup>-1</sup> 2960 (m, CH), 1738 (s, C=O), 526 (fullerene); UV-VIS λ<sub>max</sub>/nm (CH<sub>2</sub>Cl<sub>2</sub>) 257.5 (ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 1.38 × 10<sup>5</sup>), 324 (3.47 × 10<sup>4</sup>), 410 (3.30 × 10<sup>3</sup>), 421 (2.66 × 10<sup>3</sup>).

§ Selected data for **3**: Mp 91–92 °C; FAB-MS (M<sup>+</sup> + 1) 319.06227, C<sub>11</sub>H<sub>15</sub>N<sub>2</sub>O<sub>7</sub>S requires 319.06000; <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ 1.3 (s, 9H, Bu<sup>t</sup>), 7.8 (bs, 1H, NH), 8.3 (AB quart., 4H, *p*-SO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>); <sup>13</sup>C NMR (62.5 MHz, CDCl<sub>3</sub>) δ 153.6 (C=O), 151.1, 139.2, 131.1, 123.9, 29.6 (quat. C), 27.6 (Bu<sup>t</sup>); FT-IR ν<sub>max</sub>/cm<sup>-1</sup> 3282 (s, NH), 1737 (s, C=O), 1538, 1375 (s, NO<sub>2</sub>), 1346, 1162 (s, SO<sub>2</sub>).

¶ Selected data for **5**: FAB-MS (M<sup>+</sup> + 1) 1022.12920, C<sub>73</sub>H<sub>20</sub>NO<sub>7</sub> requires 1022.12398; <sup>13</sup>C NMR (62.5 MHz, CS<sub>2</sub>-<sup>2</sup>[H]<sub>6</sub>acetone) δ 153.8 (C=O), 143.9 (4C), 143.8 (4C), 143.5 (4C), 143.4 (2C), 143.2 (4C), 142.7 (2C),

142.5 (8C), 141.9 (4C), 141.8 (4C), 141.4 (2C), 141.0 (8C), 139.7 (4C), 139.1 (4C), 139.0 (4C), 107.9 (quat. C), 106.9 (quat. C), 95.0 (CH), 79.5 (2C), 69.8 (CH), 69.7 (CH), 69.1 (CH), 65.5 (CH), 64.3 (CH), 24.8 (Me), 24.7 (Me), 23.5 (Me), 23.2 (Me); FT-IR ν<sub>max</sub>/cm<sup>-1</sup> 1750 (s, C=O), 527 (fullerene).

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