

Bisazafulleroids

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The reactions of C_{60} with $N_3(CH_2)_nN_3$ ($n = 2$ or 3) in refluxing chlorobenzene give the corresponding bisazafulleroids **1** and the addition occurs at the two five–six-membered ring junctions of the same five-membered ring.

Although derivatization of C_{60} by cycloaddition reactions has been extensively investigated,¹ the regioselective multiple functionalization of C_{60} remains a challenging problem. A recent report² on the selective sequential cyclopropanation–Diels–Alder reaction of C_{60} prompted us to report our synthesis of bisazafulleroids **1**.

Two types of addition of organic azides to C_{60} are known.^{3,4} When an alkyl azide is used, the addition reaction occurs at the five–six-membered rings junction to give an azafulleroid **2**.³ On the other hand, the adduct formed at the two six-membered rings junction becomes the predominant product when N_3CO_2R is employed.⁴ For example, after HPLC separation on a Buckyclutcher column I, a 1:13 mixture of the isomers **2b**[†] and **3** was obtained from the reaction of C_{60} with N_3CO_2Et . Based on these findings, we felt that bis-azides tethered by an aliphatic chain may result in the regioselective formation of **1**.

Treatment of C_{60} with an excess of $N_3CH_2CH_2N_3$ in refluxing chlorobenzene followed by usual work-up and chromatographic separation on silica gel afforded **1a** in 53% yield based on unrecovered C_{60} . The parent peak at m/z 776 for **1a** was observed by electrospray ionization mass spectrometry in the negative ion mode (ESI-MS).⁵ The 1H NMR spectrum exhibited a typical AA'BB' pattern centred at δ 4.79. The ^{13}C NMR spectrum for **1a**[†] exhibited 28 signals in the range δ 134–153 due to two-carbon absorptions and four signals (a–d) at δ 137.29, 141.21, 143.33, 143.56 due to one-carbon absorptions. The carbon atoms for the ethylene bridge appeared at δ 50.40. These data are consistent with a structure of C_s symmetry having an azafulleroid skeleton rather than aziridino moieties and the addition may occur at the two five–six-membered ring junctions of the same five-membered ring. In addition to the possible structure **1a**, an alternative skeleton **4a**

where the addition reaction may occur at the two five–six-membered ring junctions of different five-membered moieties (or of the same six-membered ring) could not be ruled out completely. However, differentiation of these two possible structures **1a** vs. **4a** could be possible by considering the relative ^{13}C chemical shifts of one-carbon absorptions (a–d). Although it is not possible at this stage to assign all the ^{13}C chemical shifts for this adduct, the absorptions due to these single carbon atoms are characteristic. It is noted that the ^{13}C signals for certain carbon atoms in various C_s - or C_{2v} -symmetry fullerene derivatives **5** which are relatively remote from the heteroatom substituents (such as a–d) appear in a quite narrow region (within 3 ppm). The span in ^{13}C absorptions of a C_{60} derivative, where some of the carbon atoms are in proximal position to the heteroatom substituent, are in a larger range (ca. 5–7 ppm). For example, the one-carbon absorptions for **2b** occur in the range δ 138.5–143.8 and a similar observation was found in **2a**.³ Based on these reference points, we infer that the bisazafulleroid has the structure **1a**. Bisazafulleroid **1b** was prepared similarly in 31% yield from the reaction of C_{60} with $N_3(CH_2)_3N_3$. 1H NMR absorptions occurred at δ 2.49 (dtt, J 15.2, 3.2, 2.0 Hz, 1H), 3.46 (dtt, J 15.2, 12.4, 5.2 Hz, 1H) and 4.15–4.35 (m, 4H). The ^{13}C NMR spectrum for **1b**[†] exhibited 32 signals in the range δ 135–148.

The UV–VIS spectra for **1a**, **1b** and **2b** are shown in Fig. 1. Interestingly, the absorptions in the visible region appear to be similar to that of C_{60} . We have previously demonstrated that various cycloadducts at two six-membered rings junction of C_{60} exhibit significant enhancement in fluorescence emission at ca. λ_{max} 702 nm in comparison with that of C_{60} .^{4a,6} The bisazafulleroids **1**, on the other hand, showed much weaker fluorescence than that of C_{60} . Presumably, the conjugation behaviour of **1** is similar to that of C_{60} .

In summary, we have demonstrated the first regioselective synthesis of bisazafulleroids **1**. The application of this strategy for the synthesis of other fullerene derivatives is in progress.

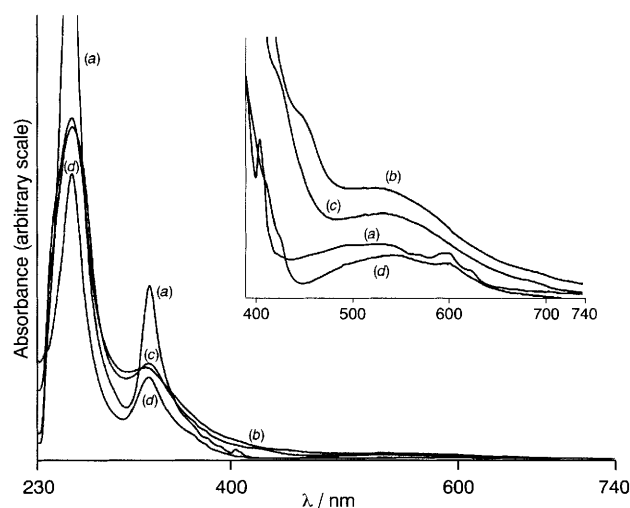
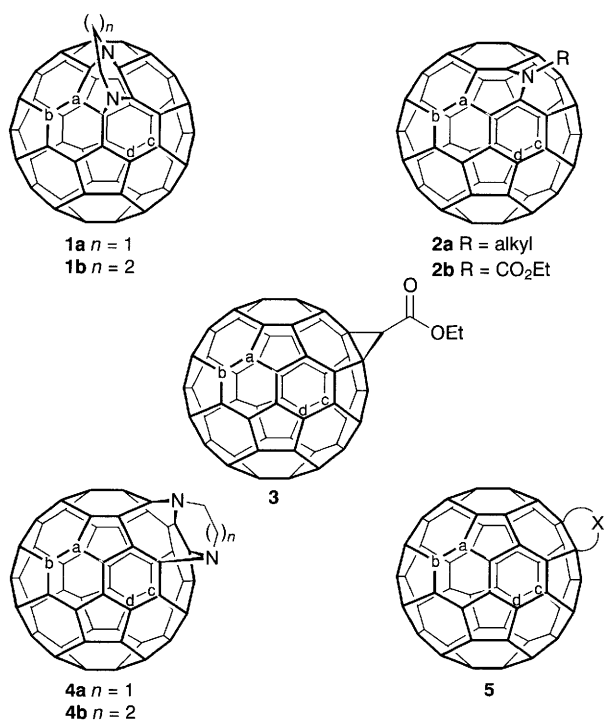


Fig. 1 The UV–VIS spectra of (a) C_{60} , (b) **1a**, (c) **1b** and (d) **2b** in $CHCl_3$. The molar absorptivities ($10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) are 115.6 at 260, 31.3 at 326, 4.2 at 450 and 2.5 at 519 nm for **1a**; 112.5 at 260, 32.7 at 329, 5.2 at 423 and 2.0 at 530 nm for **1b**; 97.0 at 260, 27.9 at 329, 2.6 at 412, 1.4 at 427, 1.0 at 544 nm and 0.8 at 598 nm for **2b** ($c = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$); Insert: spectra at a concentration of $5.0 \times 10^{-5} \text{ mol dm}^{-3}$.

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† Selected physical data: **1a**: ^{13}C NMR data [100 MHz, CS_2 , CDCl_3 , 0.03 mol dm^{-3} $\text{Cr}(\text{acac})_3$] δ 152.46 (2), 148.21 (2), 147.07 (2), 146.09 (2), 145.96 (2), 145.93 (2), 145.41 (2), 145.39 (2), 144.63 (2), 144.61 (2), 144.59 (2), 144.41 (2), 143.90 (2), 143.62 (2), 143.56 (1), 143.33 (1), 142.92 (2), 141.58 (2), 141.21 (1), 141.03 (2), 140.85 (2), 140.64 (2), 140.16 (2), 140.01 (2), 139.30 (2), 139.21 (2), 139.15 (2), 138.30 (2), 137.67 (2), 137.29 (1), 136.60 (2), 134.19 (2), 50.40 (2c). HRMS (DEI) m/z 776.0338; Calc. for $\text{C}_{62}\text{H}_4\text{N}_2$ m/z 776.0374.

1b: ^{13}C NMR data [100 MHz, CS_2 , CDCl_3 , 0.03 mol dm^{-3} $\text{Cr}(\text{acac})_3$] δ 147.78 (2), 146.63 (2), 146.49 (2), 146.06 (2), 145.75 (2), 145.65 (2), 145.24 (2), 145.21 (2), 144.88 (2), 144.59 (2), 144.34 (2), 143.97 (2), 143.57 (1), 143.55 (2), 143.54 (1), 143.49 (2), 143.39 (1), 142.82 (2), 141.98 (2), 141.77 (2), 141.67 (2), 141.04 (2), 140.94 (2), 140.79 (2), 140.51 (2), 139.86 (2), 139.30 (2), 139.08 (2), 138.74 (1), 138.33 (2), 136.02 (2), 135.58 (2), 51.39 (2), 29.88 (1c). HRMS (DEI) m/z 790.0532; Calc. for $\text{C}_{63}\text{H}_6\text{N}_2$ m/z 790.0531.

2b: ^{13}C NMR data [100 MHz, CS_2 , CDCl_3 , 0.03 mol dm^{-3} $\text{Cr}(\text{acac})_3$] δ 147.25 (2), 145.51 (2), 144.71 (2), 144.31 (2), 144.26 (2), 144.10 (2), 144.04 (2), 144.01 (4), 143.84 (4), 143.82 (1), 143.48 (2), 143.32 (1), 143.30 (2), 143.06 (2), 143.00 (2), 142.83 (2), 142.73 (2), 142.62 (2), 141.66 (2), 141.34 (2), 139.70 (2), 139.18 (2), 139.11 (1), 138.49 (1), 138.36 (2), 137.59 (2), 137.27 (2), 135.99 (2), 134.67 (2), 134.18 (2), 63.14 (1), 14.47 (1c). ESI-MS m/z 807.

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