Bisazafulleroids

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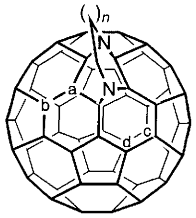
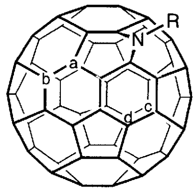
The reactions of C_{60} with $N_3(CH_2)_nN_3$ (n = 2 or 3) in refluxing chlorobenzene give the corresponding bisazafulleroids **1** and the addition occurs at the two five–six-membered ring junctions of the same five-membered ring.

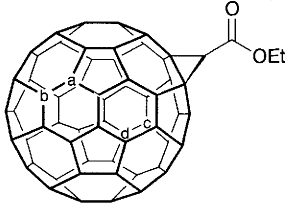
Although derivatization of C_{60} by cycloaddition reactions has been extensively investigated,[1] the regioselective multiple functionalization of C_{60} remains a challenging problem. A recent report[2] on the selective sequential cyclopropanation–Diels–Alder reaction of C_{60} prompted us to report 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.


1a *n* = 1
1b *n* = 2


2a R = alkyl
2b R = CO_2Et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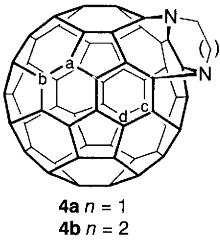
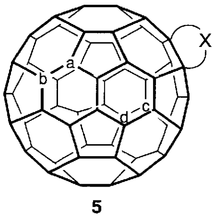

4a *n* = 1
4b *n* = 2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The UV–VIS spectra for **1a**, **1b** and **2b** are shown in Fig. 1. Interestingly, the absorptions in the visible region appear to be similar to that of C_{60}. We have previously demonstrated that various cycloadducts at two 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.

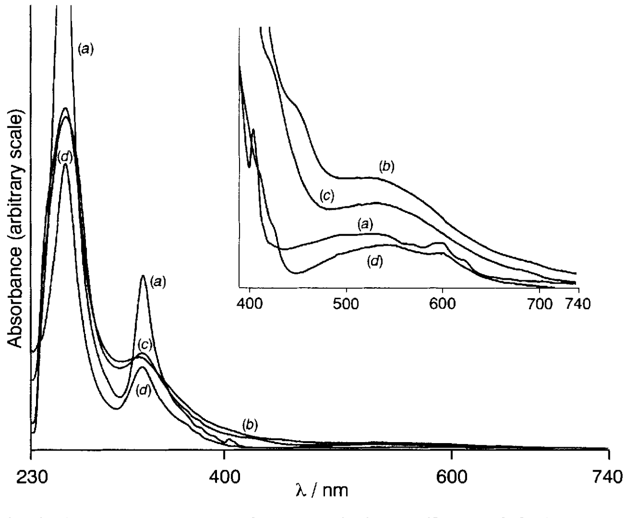

Fig. 1 The UV–VIS spectra of (*a*) C_{60}, (*b*) **1a**, (*c*) **1b** and (*d*) **2b** in $CHCl_3$. The molar absorptivities (10^3 dm^3 mol^{-1} cm^{-1}) are 115.6 at 260, 31.3 at 326, 4.2 at 450 and 2.5 at 519 nm for **1a**; 112.5 at 260, 32.7 at 329, 5.2 at 423 and 2.0 at 530 nm for **1b**; 97.0 at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

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Footnote

† *Selected physical data*: **1a**: ^{13}C NMR data [100 MHz, CS_2, $CDCl_3$, 0.03 mol dm^{-3} Cr(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 $C_{62}H_4N_2$ *m/z* 776.0374.

1b: ^{13}C NMR data [100 MHz, CS_2, $CDCl_3$, 0.03 mol dm^{-3} Cr(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 $C_{63}H_6N_2$ *m/z* 790.0531.

2b: ^{13}C NMR data [100 MHz, CS_2, $CDCl_3$, 0.03 mol dm^{-3} Cr(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.

References

1 K. M. Creegan, J. L. Robbins, W. K. Robbins, J. M. Millar, R. D. Sherwood, P. J. Tindall, D. M. Cox, A. B. Smith, III, J. P. McCauley, Jr., D. R. Jones and R. T. Gallagher, *J. Am. Chem. Soc.*, 1992, **114**, 1103; Y. Elemes, S. K. Silverman, C. Sheu, M. Kao, C. S. Foote, M. M. Alvarez and R. L. Whetten, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 351; T. Suzuki, Q. Li, K. C. Khemani, F. Wudl and Ö. Almarsson, *Science*, 1991, **254**, 1186; F. Wudl, T. Suzuki, Q. Li and K. C. Khemani, *J. Am. Chem. Soc.*, 1992, **114**, 7301, 11656; L. Isaacs, A. Wehrsig and F. Diederich, *Helv. Chim. Acta*, 1993, **76**, 1231; A. B. Smith, III, R. M. Strongin, L. Brard, G. T. Furst, W. J. Romanow, K. G. Owens and R. C. King, *J. Am. Chem. Soc.*, 1993, **115**, 5829; S. H. Friedman, D. L. DeCamp, R. P. Sijbesma, G. Srdanov, F. Wudl and G. L. Kenyon, *J. Am. Chem. Soc.*, 1993, **115**, 6506; S. H. Friedman, D. L. DeCamp, R. P. Sijbesma, G. Srdanov, F. Wudl, G. L. Kenyon and J. A. Castoro, *J. Am. Chem. Soc.*, 1993, **115**, 6510; K. L. Wooly, C. J. Hawher, J. M. J. Frechét, F. Wudl, G. Srdanov, S. Shi, C. Li and M. Kao, *J. Am. Chem. Soc.*, 1993, **115**, 9836; A. Vassela, P. Uhlmann, C. A. A. Waldraff, F. Diederich and C. Thilgen, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1388; M. Prato, A. Bianco, M. Maggini, G. Scorrano, C. Toniolo and F. Wudl, *J. Org. Chem.*, 1993, **58**, 6548; W. Ando and T. Akasaka, *J. Am. Chem. Soc.*, 1993, **115**, 1605.

2 L. Isaac, R. F. Haldimann and F. Diederich, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2339.

3 F. Wudl, M. Prato, Q. C. Li and V. Lucchini, *J. Am. Chem. Soc.*, 1993, **115**, 1148; C. J. Hawker, P. M. Saville and J. W. White, *J. Org. Chem.*, 1994, **59**, 3503; C. J. Hawker, K. L. Wooley and J. M. J. Frechet, *J. Chem. Soc., Chem. Commun.*, 1994, 925.

4 (*a*) L.-L. Shiu, K.-M. Chien, T.-Y. Liu, T.-I. Lin, G.-R. Her and T.-Y. Luh, *J. Chem. Soc., Perkin. Trans. 1*, 1994, 3355; (*b*) T. Ishida, K. Tanaka and T. Nogami, *Chem. Lett.*, 1994, **561**; (*c*) M. R. Banks, J. I. G. Cadogan, I. Gosney, P. K. G. Hodgson, P. R. R. Langridge-Smith and D. W. H. Rankin, *J. Chem. Soc., Chem. Commun.*, 1994, 1365; (*d*) M. R. Banks, J. I. G. Cadogan, I. Gosney, P. K. G. Hodgson, P. R. R. Langridge-Smith, J. R. Millar and A. T. Taylor, *Tetrahedron Lett.*, 1994, **35**, 9067.

5 T.-Y. Liu, L.-L. Shiu, T.-Y. Luh and G.-R. Her, *Rapid Commun. Mass. Spectrom.*, 1995, **9**, 93.

6 L.-L. Shiu, T.-I. Lin, S.-M. Peng, G.-R. Her, D. D. Ju, S.-K. Lin, J.-H. Hwang, C. Y. Mou and T.-Y. Luh, *J. Chem. Soc., Chem. Commun.*, 1994, 647; S.-K. Lin, L.-L. Shiu, K.-M. Chien, T.-Y. Luh and T.-I. Lin, *J. Phys. Chem.*, 1995, **99**, 105.