

Unexpected regiochemistry of a tethered bismethano[60]fullerene

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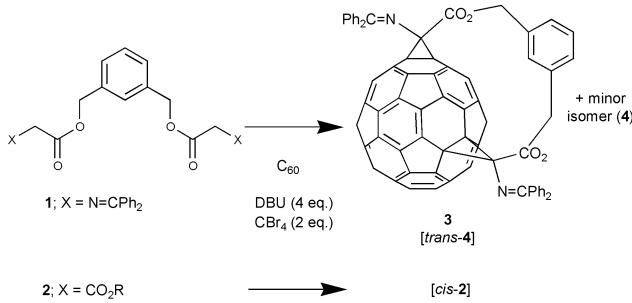
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Received (in Cambridge, UK) 27th June 2000, Accepted 1st August 2000
First published as an Advance Article on the web 22nd August 2000

The structure of a novel tethered fullerene bis-adduct, of unexpected regiochemistry, has been unequivocally assigned using INADEQUATE 2D NMR experiments.

The regioselective, multifunctionalization of C_{60} is a continuing challenge in fullerene chemistry.¹ Bis- and tris-additions to fullerenes can generally be made regioselective through the use of tethered systems.² It is not clear, however, if the regiochemical outcome of tethered reactions is solely dependent upon the nature of the tether, or the stereochemical requirements of the reactive addend, or the mechanism of addition or some combination of these factors. An additional challenge for studies in this area is the development of methods for the unequivocal assignment of the structure of bis-tethered fullerenes. Earlier structural assignments of multiple adducts have relied on comparative methods (^{13}C NMR symmetry elements and UV-vis spectroscopy).^{2e,3} However, as the production of higher order fullerene adducts increases, these methods will become less reliable, due to the decreasing symmetry of products and the lack of definitive structures for comparison. We report here the structure of a novel tethered fullerene bis-adduct of unexpected regiochemistry and the unequivocal assignment of its structure using INADEQUATE 2D NMR experiments.⁴

Earlier work has shown that tethered bis-malonate esters undergo regioselective bis-cyclopropanation reactions with C_{60} under Bingel conditions.^{2e} For example, the *meta*-substituted bis-tethered system **2** gave exclusively the *cis*-**2** regioisomer as determined by UV-vis spectroscopy and from its symmetry, determined by 1D ^{13}C NMR spectroscopy. Interestingly, the *ortho*-isomer of **2** also gives a *cis*-**2** adduct, while the corresponding *para*-isomer gives predominantly the *trans*-**4** adduct. In contrast, we have found that treatment of C_{60} with the corresponding *meta*-substituted bis-imino-glycine tethered system **1** gives, under similar reaction conditions,⁵ two regioisomeric adducts **3** and **4**⁶ in a ratio of 80:20 from 1H NMR analysis (Scheme 1). Compound **3** was obtained pure in 28% yield after separation by column chromatography and recrystallization. The 1H NMR of **3** showed resonances for the two pairs of diastereotopic methylenes at δ 5.06 and 5.71 (AB q, J_{AB} 11.2 Hz), consistent with a tethered fullerene structure. Furthermore, the MALDI-TOF spectrum of **3** showed a characteristic parent molecular ion at m/z 1297. The UV-vis spectrum of **3** showed bands in the 400–800 nm region that



Scheme 1

DOI: 10.1039/b005157h

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suggested a *trans*-**4** structure but this conclusion was not definitive due to the lack of good reference compounds. Unequivocal evidence for the structure of **3** came from ^{13}C NMR and INADEQUATE experiments.⁷

^{13}C NMR spectroscopy revealed 31 peaks associated with the fulleryl carbons in **3**. The resonance at δ 150.56 was shown to arise from the fortuitous overlap of one full-intensity peak and one half-intensity peak. Hence **3** has 32 unique fullerene carbons, four of which give half-intensity peaks (labelled as grey circles in Fig. 1), indicative of a dimethanofullerene with C_S symmetry. To distinguish between the 3 possible structural isomers, *cis*-**1**, *cis*-**2** and *trans*-**4**, INADEQUATE experiments were performed on a 10% ^{13}C enriched sample of **3**.^{8,9}

The above three possible isomers would be expected to show 2, 1 and 3 bond separations respectively, between a fulleryl sp^3 hybridized carbon and its nearest carbon on the plane of symmetry (*i.e.* half-intensity peak). These experiments revealed a 3-bond connectivity (shown as grey lines in Fig. 1) between C1 (sp^3 carbon) and C19 (half-intensity peak) providing unequivocal evidence for its *trans*-**4** structure. Starting from C19, correlations were observed to the other half-intensity peak (C20) with a relatively large coupling constant ($^1J_{CC}$ = 66.8 Hz) typical for 6,6 ring fusion carbons and one to C5 with a smaller $^1J_{CC}$ (57.2 Hz) typical for 6,5 ring fusion carbons.⁴ C5 showed correlations to C6 ($^1J_{CC}$ = 73.1 Hz) and C4 ($^1J_{CC}$ = 53.2 Hz), consistent with their 6,6 and 5,6 ring fusion positions, as well as to C19. C6 showed a correlation to the sp^3 carbon C1, unequivocally confirming the position of the cyclopropane ring to the plane of symmetry. Further corroborative evidence for this structure was the observation that C4 showed only 2 correlations (to C3 and C5) consistent with the magnetic

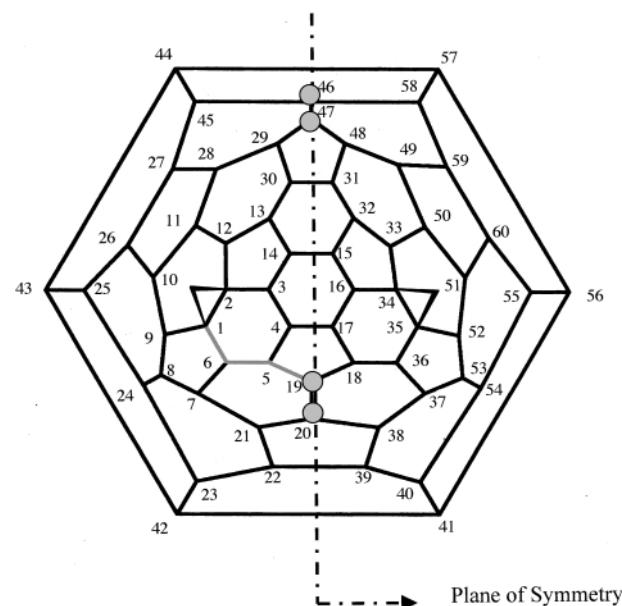


Fig. 1 Schlegel diagram of **3** (tether not shown) with carbons that lie on the plane of symmetry shown as grey circles.

Table 1 Chemical shifts (δ), peak assignments, and carbon–carbon coupling constants ($^1J_{CC}$) for the [60]fullerene cage of **3** (^{13}C -enriched)⁷

Carbon Number	δ (ppm)	(Carbon number) $^1J_{\text{C}-\text{C}}$ /Hz
1,35	81.37	(2), ^b (6) 44.5, (9) 44.5
2,34	81.25	(1), ^b (3) 40.8, (12) 41.2
3,16	145.73	(2) 40.8, (4) 69.9, (14) 58.8
4,17	129.04	(3) 69.9, (5) 53.2
5,18	136.24	(4) 53.2, (6) 73.1, (19) 57.2
6, ^a 36	150.56	(1) 44.5, (5) 73.1, (7) 56.8
7,37	146.49	(6) 56.8, (8), ^b (21) 67.2
8,53	146.4	(7), ^b (9) 56.0, (24) 67.2
9,52	149.6	(1) 44.5, (8) 56.0, (10) 72.3
10,51	147.13	(9) 72.3, (11) 53.0, (26) 56.8
11,50	136.24	(10) 53.0, (12) 71.1, (28) 57.2
12,33	146.55	(11) 71.1, (13) 56.4, (2) 41.2
13,32	145.28	(12) 56.4, (14) 54.4, (30) 68.0
14,15	143.52	(13) 54.4, (15) 58.8
19, ^c	142.21	(5) 57.2, (20) 66.8
20, ^c	148.68	(19) 66.8, (21) 56.4
21,38	139.39	(7) 67.2, (20) 56.4, (22) 56.8
22, ^{39b}	141.11	(21) 56.8, (23), ^b
23, ^{40b}	141.28	(22), ^b (24), ^b (42) 56.4
24,54	140.89	(8) 67.2, (23), ^b (25) 56.4,
25,55	141.29	(24) 56.4, (26) 68.3, (43) 55.6
26,60	143.39	(10) 56.8, (25) 68.3, (27) 55.2
27,59	148.31	(26) 55.2, (28) 55.2, (44/45) 68.3
28,59	140.31	(11) 57.2, (27) 55.2, (29) 68.0
29,48	145.28	(28) 68.0, (30) 56.4, (47) 54.4
30,31	138.72	(29) 56.4, (13) 68.0
42,41	141.82	(23), ^b (43) 54.8
43,56	145.54	(25) 55.6, (42) 54.8, (44/45), ^b
44,57	145.46	(11), ^b (45), ^b
45,58	145.46	(27) 68.3, (44), ^b (46) 56.0
46, ^a c	150.56	(45) 56.0, (47) 68.0
47, ^c	145.73	(46) 68.0, (29) 57.2

^a Denotes peak has two resonances, one full-intensity and one half-intensity. ^b Denotes coupling is not first order; peak positioning is consistent with structure model. ^c Denotes half-intensity peaks.

equivalence of C4 and C17 due to their positions relative to the plane of symmetry.

Using the above methods we have assigned all carbons in **3** and obtained information about the relative bond lengths from the measurement of $^1J_{CC}$ values (Table 1). These measured values were consistent with the radialene structure of **3**.

The regiochemical difference between our tethered reaction and that of **2** with C_{60} clearly demonstrates that much has yet to be understood about tethered fullerene reactions before generalizations on regiochemical outcomes can be made. These differences in regiochemistry may indicate that these reactions proceed *via* different mechanisms and experiments are in progress to help understand these differences.¹⁰

We thank the Australian Research Council for financial support and for a PhD scholarship to G. A. B.

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- The minor isomer **4** was obtained pure in 12% yield and has C_2 symmetry from ^{13}C NMR analysis which showed no half-intensity peaks and 30 sp^2 resonances. The possible structures for this molecule therefore are, *cis*-**3**, *trans*-**3** or *trans*-**2**. The *trans* isomers seem unlikely from PM3 calculations, leaving *cis*-**3** as the most likely structure.
- The INADEQUATE experiment was performed on a Bruker DMX 600 spectrometer fitted with a Bruker TXI-XYZ $^1\text{H}/^{13}\text{C}/^{15}\text{N}$ probe. The sample (*ca.* 16 mg) was dissolved in CS_2 - CDCl_3 6:4 (*ca.* 250 μl) in a Shigemi tube and the spectrum was recorded at 288 K. A standard pure phase (States-TPPI) double quantum spectrum with power-gated proton decoupling was employed. A spectral width of 13020.8 Hz was used in both dimensions resulting in deliberate folding in f_1 which does not cause any ambiguity of peak assignments. 2048 \times 8192 total points were collected in t_1 and t_2 respectively. A recycle delay of 9 s and 16 scans per increment were employed. The 90° pulse length was 11.6 μs .
- ^{13}C enriched (10%) C_{60} purchased from Mer Fullerenes, Arizona.
- To a solution of [60]fullerene, CBr_4 (0.54 g, 1.42 mmol) and **1** (0.47 g, 0.810 mmol) in PhCl (200 mL) was added DBU (0.43 g, 0.675 mmol), at room temperature and the solution was stirred for 2 h. The crude material was filtered through a short plug of silica, eluting first with toluene (to retrieve unreacted [60]fullerene) and then with CH_2Cl_2 (DCM). Column chromatography eluting with (90:10; DCM-light petroleum) and recrystallised from DCM-Et₂O provided **3** (0.245 g, 28%) and **4** (0.093 g, 12%). Data for **3**: λ (DCM)/nm ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 420 (15000), 630 (250), 690 (150). δ_{H} (CDCl_3 , 400 MHz): 5.06 (d, *J* 11.2), 5.71 (d, *J* 11.2), 7.07 (t, *J* 7.6), 7.14 (s), 7.30 (t, *J* 7.6), 7.40 (t, *J* 7.2), 7.46 (t, *J* 7.2), 7.55 (t, *J* 7.2), 7.92 (d, *J* 8.4), 8.04 (d, *J* 8.4). δ_{C} (CDCl_3 , 100 MHz): 68.04, 81.47, 81.80, 97.06, 127.93, 128.04, 128.32, 129.36, 129.60, 136.42, 137.66, 138.92, 139.61, 140.60, 140.94, 141.27, 141.33, 141.39, 141.54, 142.10, 142.48 (*ipso*), 143.64, 143.92, 145.63, 145.68, 145.75, 145.80 (1C), 145.98, 146.03 (1C), 146.65, 146.75, 146.82, 147.40, 148.62, 148.99 (1C), 149.89, 150.88 (two peaks, one full-intensity and one half-intensity), 160.71, 161.25. MALDI-TOF m/z (–ve ion mode, 9-nitroanthracene): 1296 (M-H), 720 (C_{60}^-). Data for **4**: λ (DCM)/nm ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 320 (19000), 430 (sh, 1700), 450 (sh, 1400), 640 (280), 695 (190). δ_{H} (CDCl_3 , 400 MHz): 5.31 (d, *J* 11.2), 5.41 (d, *J* 11.2), 6.95 (s), 7.23 (t, *J* 7.6), 7.37 (dd, *J* 7.2, 1.6), 7.50 (dd, *J* 7.6, *J* 1.2), 7.62 (t, *J* 8.4), 8.17 d, *J* 7.6), 8.21 (d, *J* 7.6). δ_{C} (CDCl_3 , 100 MHz): 68.46, 81.83, 82.38, 96.02, 128.32, 128.56, 129.64, 129.94, 131.37, 134.55, 134.77, 138.49, 139.24, 140.71, 141.02, 141.20, 141.84, 143.36, 143.46, 143.98, 144.06, 144.11, 144.30, 144.42, 144.70, 144.92, 145.00, 145.92, 147.28, 147.38, 147.51, 147.80, 148.55, 148.86, 149.01, 149.21, 150.93, 153.44, 154.37, 161.03, 161.14. MALDI-TOF m/z (–ve ion mode, 9-nitroanthracene): 1296 (M-H), 720 (C_{60}^-).
- PM3 calculations indicated little difference in heats of formation between **3** and its *cis*-**2** isomer.