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Structural Reassignment of the Mono- and Bis-Addition Products from the Addition Reactions of *N*-(Diphenylmethylene)glycinate Esters to [60]Fullerene under Bingel Conditions

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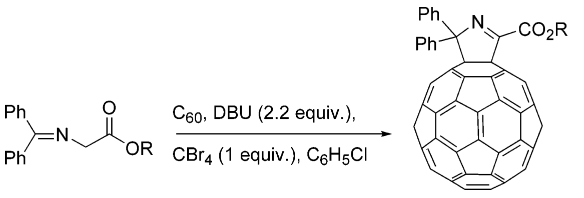
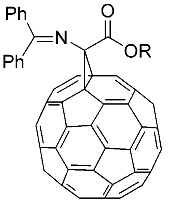


The addition of *N*-(diphenylmethylene)glycinate esters ($Ph_2C{=}NCH_2CO_2R$) to [60]fullerene under Bingel conditions gives [60]fullerenyldihydropyrroles and not methano[60]fullerenyl iminoesters [$C_{60}C(CO_2R)(N{=}CPh_2)$] as previously reported. Unequivocal evidence for the structure of $C_{60}C(CO_2Et)(N{=}CPh_2)$ was provided by INADEQUATE NMR studies on ^{13}C enriched material. New mechanistic details are proposed to account for the formation of [60]fullerenyldihydropyrroles and their reductive ring-opening reactions.

The reaction of activated methylenes (WCH_2W') with [60]fullerene in the presence of a halogenating agent and base is known as the Bingel reaction and commonly yields fused three-membered-ring adducts (methano[60]fullerenes, $C_{60}CW(W')$).[1,2] In recent papers we reported that the addition of *N*-(diphenylmethylene)glycinate esters **3a**−**d** to [60]fullerene under Bingel conditions gave methano[60]fullerenyl iminoesters **1a**−**d**, and that tethered bis-*N*-(diphenylmethylene)glycinate esters, derived from *m*- and *p*-benzenedimethanol scaffolds, gave the corresponding bis-methano[60]fullerenyl iminoesters **2**.[3−6] The structures of compounds **1a**−**d** were based upon the observation of a single sp^3 fullerene resonance (between δ 82 and 83) in the ^{13}C NMR spectra (4:6 $CDCl_3$:CS_2) of these compounds at 75 or 100 MHz, which implied to us that these molecules had C_s symmetry.



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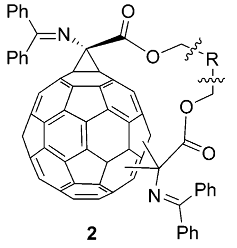
a, R = ^tBu; **b**, R = Et;
c, R = *l*-menthyl; **d**, R = $EtCO_2CH_2^-$



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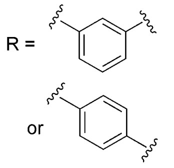
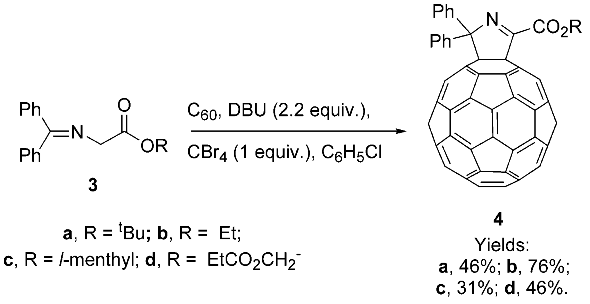


More recently we have examined the ^{13}C NMR spectra (4:6 $CDCl_3$:CS_2) of the compounds assigned structures **1a** and **1b** at higher field (150 MHz), which showed two sp^3 fullerene resonances separated by 0.02−0.03 ppm (3−4.5 Hz) in this chemical shift region. When pure $CDCl_3$ was employed as the solvent then these resonances were resolved by 16 Hz. This prompted us to reexamine our initial NMR and structural assignments and to perform INADEQUATE NMR experiments to unequivocally determine the structure of **4b**. We report here that the products of these reactions are indeed [60]fullerenyldihydropyrroles (**4a**−**d**, Scheme 1).

SCHEME 1



The ^{13}C NMR spectrum of **4b** at 150 MHz showed the presence of 28 full-intensity and 2 half-intensity sp^2 resonances (C-52 and C-60, Figure 1, Table 2) along with two sp^3 fullerene resonances (δ 82.71 and 82.73 for C-1 and C-9, not necessarily respectively, Figure 1) separated by 0.02 ppm indicating the fullerenyl sp^3 carbons lie in the plane of symmetry ruling out the possibility of a cyclopropyl ring (methano[60]fullerene). Likewise the ^{13}C NMR spectrum of **4a** at 150 MHz also showed two closely resolved sp^3 fullerene resonances at δ 82.76 and 82.73. Further diagnostic evidence was a strong HMBC correlation between the *ortho*-protons of the phenyl rings (Figure 2) of **4b** and the dihydropyrrole sp^3 carbon resonance (C_β) at 95.9 ppm (Table 1). Furthermore, no correlations were observed to any downfield resonance attributable to the imine group (at 159.7 ppm). Such a

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† University of New South Wales.
‡ University of Wollongong.
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10.1021/jo051282u CCC: \$30.25

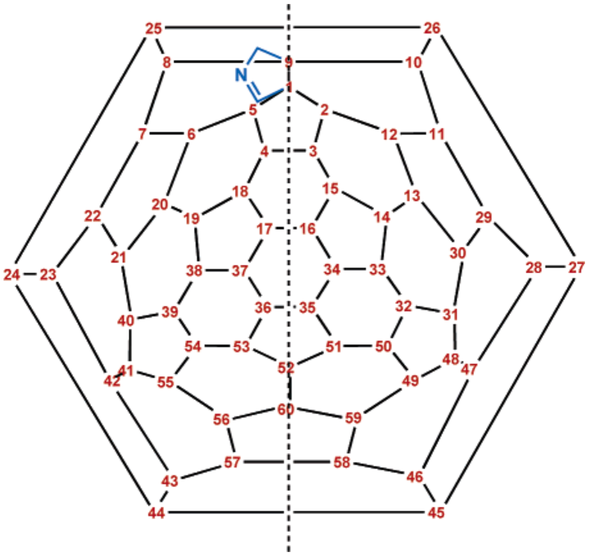


FIGURE 1. Schlegel diagram of **4b** (ester and phenyl groups omitted for clarity).

TABLE 1. HMBC Correlations

compd	H_α (ppm)	C_β (ppm)
4b, R = Et	8.10	95.85
4a, R = ^{t}Bu	8.05	96.63

correlation would have been expected for **1b** but not for **4b**. The HMBC experiments on **4a** also showed the same correlations (Figure 2, Table 1).

To unequivocally assign all the carbons in the fullerene cage 2D-INADEQUATE and ^{13}C NMR experiments were conducted on **4b** using 10% ^{13}C enriched fullerene. Fullerenyl resonances were distinguished from nonfullerenyl resonances by the presence of $^{13}C-^{13}C$ coupled satellites situated on either side of a central resonance peak. Assignment of the carbon sphere was achieved on the basis of one-bonded $^{13}C-^{13}C$ connectivities and examination of the carbon−carbon coupling ($^1J_{CC}$) values knowing typical values for C(sp^2)−C(sp^3) bonds (∼48 Hz), the longer 5,6 ring-fused bonds (54−57 Hz), and the shorter 6,6 ring-fused bonds (65−71 Hz).[7−9] This analysis facilitated the unambiguous characterization of the entire fullerene sphere as shown in Figure 1 and Table 2.

We propose that the [60]fullerenyldihydropyrroles **4a−d** arise from ring-closure of the anionic intermediate **A** (Scheme 2). Ring-closure would favor formation of a five-membered (dihydropyrrole) ring (**4a−d**) over the more strained three-membered (cyclopropane) ring (**1a−d**).

The regiochemical outcomes from tethered bis-additions to the fullerene cage remain as previously reported,[6] with symmetry arguments and UV−vis data from all the bis-substituted analogues (**5−8**) providing evidence for the regiochemical outcome with analysis of their 2D-INADEQUATE spectra unambiguously confirming their regiochemistry (Scheme 3). The symmetry of the bis-substituted fullerenyl adducts is equivalent regardless of whether the attachments are via three- or five-membered rings, therefore analysis of the ^{13}C NMR

TABLE 2. Chemical Shifts (δ), Peak Assignments, and Carbon−Carbon Coupling Constants ($^1J_{CC}$) for the [60]Fullerene Cage of 4b (150 MHz, $CDCl_3$:CS_2)

carbon no.	δ (ppm)	(carbon no.) $^1J_{C-C}$/Hz
1^{a-c}	82.71	(2) 43.4
2,5	153.06	(1) 43.4, (3) 57.1, (6) 72.4
3,4	145.02	(2) 57.1, (15) 67.6
6,12	134.55	(2) 72.4, (7) 54.2, (13) 57.3
7,11	136.53	(6) 54.2, (8) 71.3, (22) 57.2
8,10	148.49	(7) 71.3, (9) 41.5, (25) 57.5
9^{a-c}	82.73	(8) 41.5
13,20	141.71	(6) 57.3, (14) 68.0, (21) 55.6
14,19	144.73	(13) 68.0, (15) 56.4, (33) 55.5
15,18	139.08	(3) 67.6, (14) 56.4, (16) 56.4
16,17	141.69	(15) 56.4, (34) 55.8
{ 21,30^{b,c} 50,54 }	{ 145.25 145.28 }	{ (13) 55.6, (22) 55.5, (31) 68.3, (32),^{d} (49),^{d} (51)^d }
22,29	141.20	(7) 57.2, (21) 55.5, (23) 67.7
23,28	145.35	(22) 67.7, (24) 56.8, (47) 56.5
24,27	139.61	(23) 56.8, (25) 68.0, (44) 56.1
25,26	147.49	(8) 57.5, (24) 68.0
31,40	142.88	(21) 68.3, (32) 56.1, (41) 55.9
32,39	145.81	(50),^{d} (31) 56.1, (33) 68.1
33,38	144.06	(14) 55.5, (32) 68.1, (34) 55.9
34,37	142.28	(16) 55.8, (33) 55.9, (35)^d
35,36	142.65	(34),^{d} (51) 56.3
41,48	146.27	(31) 55.9, (47) 68.0, (49) 56.1
42,47	144.08	(23) 56.5, (41) 68.0, (43) 56.0
43,46	142.25	(44),^{d} (47) 56.0, (57)^d
44,45	141.76	(24) 56.1, (43)^d
49,55	144.96	(50),^{d} (41) 56.1, (56) 67.5
51,53	145.67	(50),^{d} (35) 56.3, (52) 56.4
52^a	146.79	(51) 56.4
56,59	145.82	(49) 67.5, (57) 55.9, (60) 55.9
57,58	142.62	(43),^{d} (56) 55.9
60^a	146.93	(56) 55.9

^{a} Denotes half-intensity peaks. ^{b} Denotes peak overlap. ^{c} Unable to differentiate. ^{d} $^1J_{C-C}$ values could not be accurately measured.

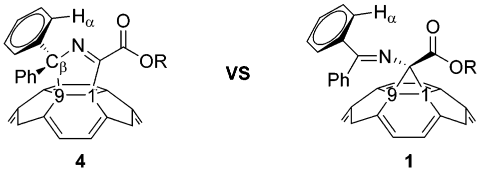
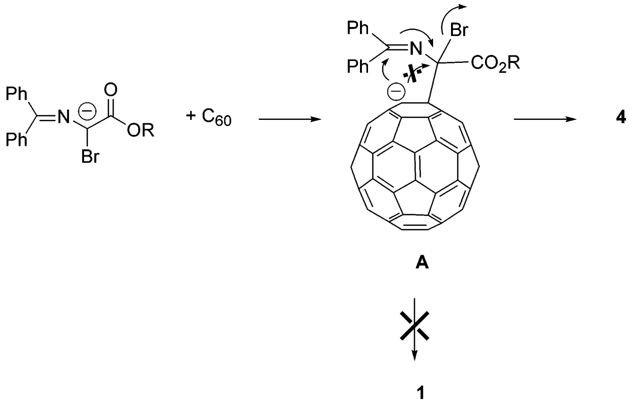


FIGURE 2.

SCHEME 2



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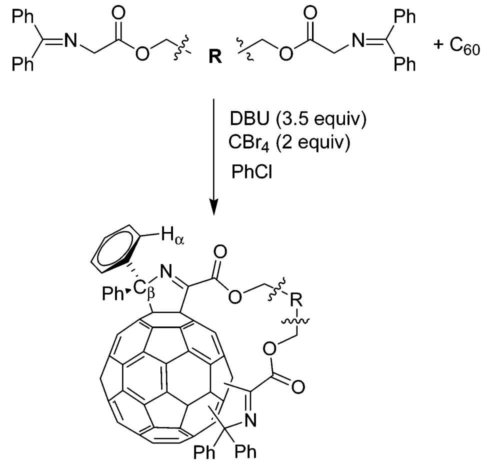
SCHEME 3



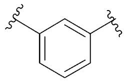
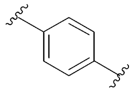
R	Regiochemistry and yield (%)	
	(**5**) *trans-4* (32)	(**6**) *cis-3* (10)
	(**7**) *trans-3* (37)	(**8**) *trans-4* (10)

TABLE 3. HMBC Correlations

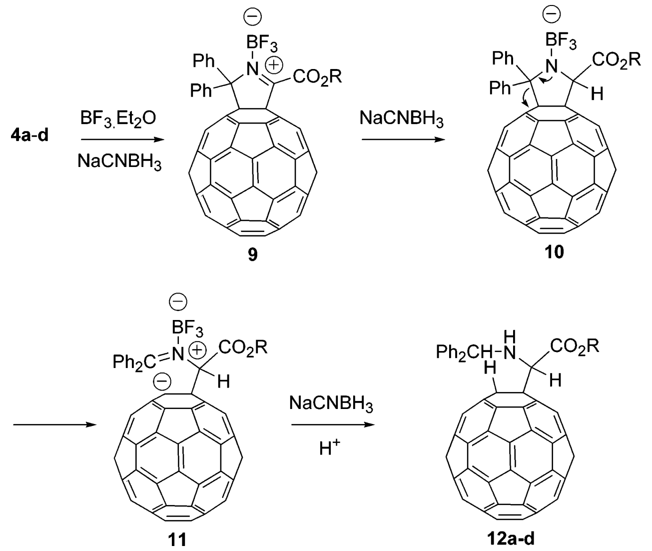
compd	H$_\alpha$^{a} (ppm)	C$_\beta$ (ppm)
5	8.04, 7.92	97.06
6	8.21, 8.17	96.02
7	8.25, 8.09^b	95.94^b
8	8.02, 7.92	96.74

[a] The two phenyl groups on the dihydropyrrole are not equivalent in bis adducts, as the symmetry plane no longer bisects C$_\beta$. [b] Due to the poor solubility of this compound in organic solvents it was trans-esterified to the corresponding ethyl ester to facilitate spectral acquisition.

spectra could not differentiate between the two possible structures. However, reexamination of the HMBC correlations showed that all bis-substituted fullerenyl adducts were the corresponding bis-[60]fullerenyldihydropyrroles (**5**−**8**) and not the previously reported bis-methano[60]fullerenes. Table 3 summarizes the HMBC correlations observed for each bis-adduct previously reported with the reassigned structures shown in Scheme 3.

These new structural assignments help explain the difference in regiochemical outcomes between tethered bis-malonate esters[10] and our bis-*N*-(diphenylmethylene)-glycinate esters, both of which were derived from *m*- and *p*-benzenedimethanol scaffolds and reacted with [60]-fullerene under Bingel conditions. These differences in regiochemistry can now be understood in terms of their different reaction mechanisms and the geometry of the intermediate monoadduct.

SCHEME 4



Reductive ring-opening products of compounds **4a**−**d** with sodium cyanoborohydride, the 1,2-dihydro[60]-fullerenylglycinates **12a**−**d**, are correct as previously published (Scheme 4). However, in light of these recent findings the proposed reaction mechanism requires adjustment. The proposed intermediate **10** (Scheme 4) undergoes ring-opening to give the more conjugated (stable) diphenylmethyleneimine, fullerenyl anion intermediate **11**, rather than the less conjugated Ph$_2$CHN=C(fullerenyl)(CO$_2$R) imine, fullerenyl anion intermediate (not shown). Further reduction of the imine moiety of **11** and protonation gives the 1,2-dihydro[60]fullerenylglycinates **12a**−**d**.

In conclusion, the addition of *N*-(diphenylmethylene)-glycinate esters to [60]fullerene under Bingel conditions gives [60]fullerenyldihydropyrroles and not methano[60]-fullerenyl iminoesters as we previously reported. Unequivocal evidence for the structure of C$_{60}$C(CO$_2$Et)(N=CPh$_2$) was provided by INADEQUATE NMR studies on ^{13}C enriched material. New mechanistic details have been proposed to account for the formation of [60]fullerenyldihydropyrroles and their reductive ring-opening reactions.

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Supporting Information Available: Copies of the ^{13}C, HMBC, and INADEQUATE NMR spectra of **4b** and the ^{13}C NMR spectrum of the sp^3 fullerene region of **4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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