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Regioselective formation of highly functionalised heterofullerenes: pentamalonates of $RC_{59}N$ involving an octahedral addition pattern

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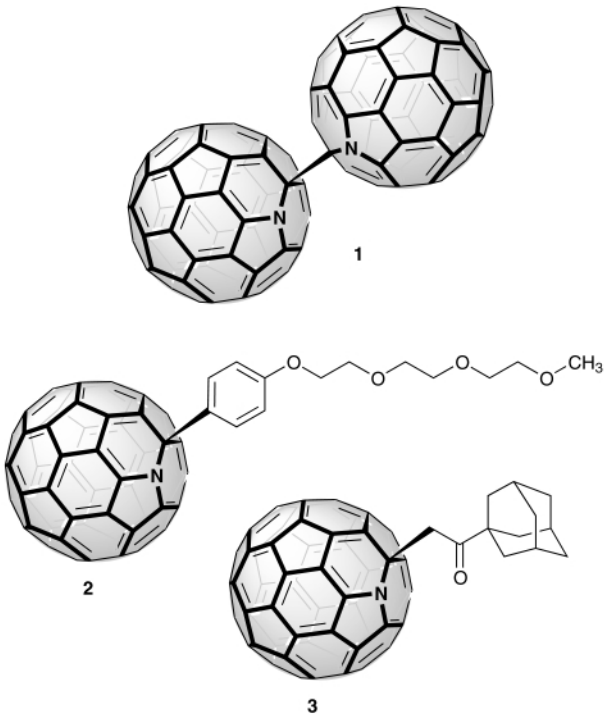
The treatment of monomeric azafullerene derivatives $RC_{59}N$ with an excess of diethyl bromomalonate in the presence of DBU and dimethylanthracene leads to the regioselective formation of azafullerene pentamalonates with an octahedral C_s symmetrical addition pattern.

The organic chemistry of the parent azafullerene $C_{59}N$ in the form of its dimer **1**[1] has been so far restricted to the synthesis of monoadducts $RC_{59}N$. In these azafullerene derivatives the addend R is always bound to the cluster C-atom which forms a [6,6]-bond to the heteroatom.[2–5] We have shown recently, that monomeric derivatives $RC_{59}N$ such as **2** and **3** are easily



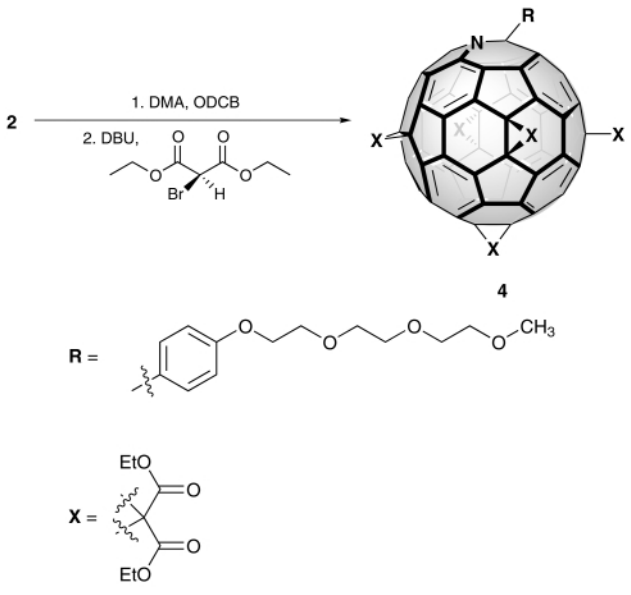
available by treatment of the dimer **1** with electron rich aromatics or enolizable carbonyl compounds in the presence of oxygen and *p*-TsOH.[3–5] The only example of a multiple adduct of $C_{59}N$ is the tetrachloride $Cl_4ArC_{59}N$ containing a pyrrole moiety within the fullerene cage.[6]

Here we report on the first multiple functionalisation of $C_{59}N$ with organic addends. As a model reaction the template mediated generation of oligomalonates, which we developed for the highly regioselective functionalisation of octahedral sites within C_{60} has been chosen.[7] This approach allows us to synthesize pentakisadducts of $RC_{59}N$ containing a C_s symmetrical addition pattern and a cage π-electron system consisting of eight isolated benzenoid rings.

After stirring a solution of the monoadduct **2** and a fivefold excess of dimethylanthracene (DMA) in 1,2-dichlorobenzene (ODCB) for 3 h, a tenfold excess of DBU and diethyl bromomalonate was added (Scheme 1). After stirring this reaction mixture for 2 days a colour change of the olive green solution into orange was observed.

After purification by HPLC using a Buckyclutcher column and toluene–ethyl acetate (8:2) as eluent, the pentamalonate **4** was obtained in 20% yield. The other regioisomeric multi-adducts could not be separated by chromatographic methods.

The complete structural characterisation of **4** was carried out by ^{1}H NMR, ^{13}C NMR, UV-Vis and FT-IR spectroscopy as well as by mass spectrometry.† The ^{1}H NMR spectrum shows two doublets for the aromatic AB spin system at δ 7.95 and 7.00. The methyl group of the polyether side chain resonates as a singlet at δ = 3.31. The signals for the methylene groups of the polyether side chain are found in the region between δ = 4.25–3.45. The four different methylene groups of the malonate function resonate as a broad multiplet at δ = 4.2 and the signals for the four different methyl groups of the malonate function can be found as a broad multiplet at δ = 1.25. The determination of the symmetry was unambiguously carried out by ^{13}C NMR spectroscopy. The ^{13}C NMR spectrum of **4** (Fig. 1) shows five signals for the ten carbonyl groups at δ = 164 with one signal showing double intensity. For a C_s symmetrical pentamalonate six signals are expected. In the sp^2 region between δ = 115–160 28 signals are found, four of which belong to the aromatic addend. The remaining 24 signals are due to the sp^2 C-atoms of the C_s symmetrical fullerene cage. The most striking evidence for a C_s symmetrical adduct can be found in the region between δ = 42–48 where four signals appear, one having double intensity. These are the signals of the methano C-atoms of the malonate bridges. Three of those C-atoms are located on the mirror plane of the molecule giving rise to three



Scheme 1

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well resolved signals. The other two methano C-atoms in equatorial positions are chemically equivalent due to the C_s plane, causing the appearance of just one signal with double intensity. The C-atoms of the methylene groups give rise to just one signal at δ = 62.81 and one signal at δ = 45.37. The methyl groups of the malonate addends resonate at δ = 14.04. The signals of the six different fullerene sp^3 C-atoms and the sp^3 C-cage atom which is adjacent to the N-atom appear as seven different signals in the region between δ = 62.81–77.88. The UV-Vis spectrum of the orange pentakisadduct **4** is completely different from those of monomeric derivatives $RC_{59}N$.[2–5] The characteristic fullerene absorption at λ_{max} = 320 nm has disappeared. Similarly to hexakisadducts of C_{60} containing a T_h-symmetrical addition pattern[7] the most intensive absorption is shifted to λ_{max} = 281 nm.

The reaction of the adamantyl derivative **3** applying the same reaction conditions afforded compound **5**. The structural characterisation of this azafullerene derivative was carried out by ^{1}H NMR, ^{13}C NMR, UV-Vis and FT-IR spectroscopy. In the ^{13}C NMR spectrum no symmetry can be detected; *e.g.* each of the five methano C-atoms gives an individual signal in the region between δ = 42–48. The FAB-MS clearly shows a peak for M^+ at *m/z* 1769. This peak displays the characteristic Br isotope pattern. In the ^{1}H NMR spectrum the methine proton resonates at δ = 5.6, which is characteristic for an α-bromo ketone. Again the resonances for the methylene protons of the malonate addends can be found in the region between δ = 4.1–4.5 forming a broad multiplet. The individual protons for the adamantyl group resonate in the region between δ = 1.2–2.0 and the methyl groups of the malonate addends can be found as a broad multiplet at δ = 1.3. Significantly, the UV-Vis spectrum of **5** is similar to that of **4**, indicating that the same addition patterns are involved. Obviously, the five-fold cyclopropanation of **3** in octahedral positions is accompanied by bromination of the methylene group of the ketone addend. As a consequence, a chiral center is introduced, which causes symmetry lowering to C_1. The facile formation of **5** clearly demonstrates that the α-methylene protons of azafullerenated ketones such as **3** are very acidic. Their deprotonation with DBU used as base generates an intermediate enolate which is able to attack diethyl bromomalonate to efficiently form an α-brominated ketone.

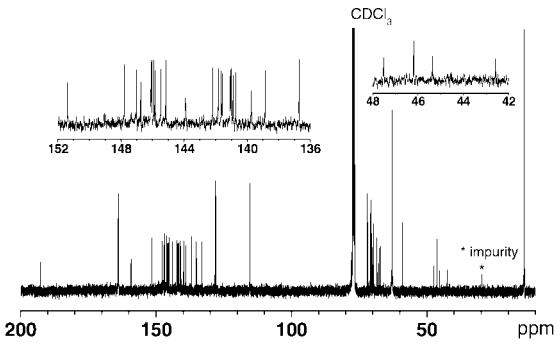
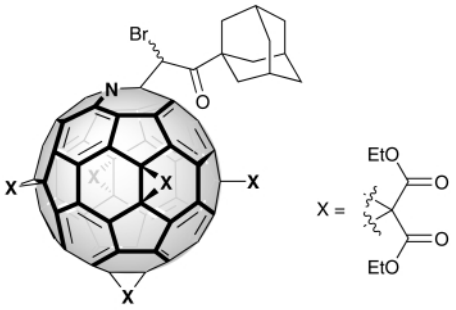


Fig. 1 100 MHz ^{13}C NMR spectrum of **4**.



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Notes and references

† Selected data for compound **4**: ν(KBr)/cm^{-1} 2979, 2932, 2904, 2872, 1744, 1608, 1509, 1464, 1459, 1391, 1368, 1252, 1221, 1178, 1095, 1021, 857, 710, 667 and 532; $\lambda_{max}(CH_2Cl_2)$/nm 265, 281, 514; ^{13}C NMR δ (100 MHz, $CDCl_3$) 163.96 (C=O, 2C), 163.81 (C=O, 4C), 163.78 (C=O, 2C), 163.73 (C=O, 1C), 163.70 (C=O, 1C), 159.19 (Ar–C–O, 1C), 151.41, 147.80, 147.04, 146.76, 146.11, 146.08, 145.93, 145.85, 145.49,145.17, 143.92, 142.19, 141.85, 141.66, 141.59, 141.09, 141.04, 140.92, 140.72, 139.75, 138.87, 136.73, 135.23, 134.83, 132.97, 127.96 (Ar–C, 2C), 115.21 (Ar–C, 2C), 77.88, 71.93, 70.87, 70.67, 70.58, 70.44, 70.14, 69.91, 69.68, 68.50, 68.29, 67.64, 67.07, 62.81 (–OCH_2CH_3, 8C), 62.71 (–OCH_2CH_3, 2C), 59.03 (–OCH_3, 1C), 47.52 (1C), 46.20 (2C), 45.37 (1C), 42.59 (1C), 14.04 (–CH_3, 10C); ^{1}H NMR δ (400 MHz, $CDCl_3$) 7.95 (d, 2H, ^3J = 8.8 Hz, Ar–H), 7.00 (d, 2H, ^3J = 8.8 Hz, Ar–H), 4.24 (br m, 24 H, –O*C*H_2CH$_3$ + 2 × –O*C*H_2CH$_2$), 3.84 (m, 2H, –O*C*H_2CH$_2$), 3.70 (m, 2H, –O*C*H_2CH$_2$), 3.64 (m, 2H, –O*C*H_2CH$_2$), 3.61 (m, 2H, –O*C*H_2CH$_2$), 3.49 (m, 2H, –O*C*H_2CH$_2$), 3.31 (s, 3H, −OCH_3), 1.25 (br m, 30 H, –CH_3); *m/z* (FAB) 1752 (M^+ + H), 1707 (M^+ + H – OEt), 1595 (M^+ – $C(CO_2Et)_2$ + 2H), 722 ($C_{59}N$). Selected data for compound **5**: ν(KBr)/cm^{-1} 2981, 2930, 2907, 2852, 1746, 1635, 1451, 1447, 1392, 1368, 1263, 1221, 1094, 1072, 1022, 858, 711, 669, 539, 528 and 511; $\lambda_{max}(CH_2Cl_2)$/nm 268, 285, 312, 501; ^{13}C NMR δ (100 MHz, $CDCl_3$) 207.01 (C=O, 1C), 163.60–163.90 (C=O, 10C), 152.41, 152.11, 147.51, 147.28, 147.26, 147.20, 146.81, 146.63, 146.58, 146.49, 145.98, 145.93, 145.89, 145.76 (2C), 145.70, 145.61, 145.55, 145.13, 145.08, 143.88, 143.85, 143.64, 142.79, 142.32, 142.27, 141.97, 141.86, 141.61, 141.58, 141.15, 141.08, 140.78 (2C), 140.66 (2C), 139.85, 139.83, 138.36, 138.24, 137.87, 137.77, 137.01, 136.99, 135.36, 135.27, 133.60, 133.13, 77.70 (1C), 70.39, 70.30, 69.88, 69.80, 68.42, 68.29, 67.16, 67.12, 62.82–62.71 (–OCH_2CH_3, 10C), 62.67 (–CHBr–, 1C) 48.17, 47.89, 47.55, 46.07, 45.36, 42.65, 38.40, 36.22, 27.78, 14.13–13.86 (–CH_3, 10C); ^{1}H NMR δ (400 MHz, $CDCl_3$) 5.62 (s, 1H), 4.36–4.19 (br m, 24 H, –O*C*H_2CH$_3$), 2.02 ('d', 6 H), 1.89 ('d', 3H), 1.72 (dd, 6H), 1.33–1.19 (br m, 30 H, –CH_3); *m/z* (FAB) 1767 and 1769 (M^+), 1722 and 1724 (M^+ − OCH_2CH_3), 1689 (M^+ − Br), 1513, 722 ($C_{59}N$).

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