

Facile synthesis of arylated heterofullerenes ArC₅₉N

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The thermal treatment of the heterofullerene dimer (C₅₉N)₂ with anisole, toluene and 1-chloronaphthalene in the presence of toluene-*p*-sulfonic acid and air leads to the formation monoarylated azafullerenes ArC₅₉N in very good yields.

The simplest nitrogen heterofullerene C₅₉N is a reactive radical intermediate and stabilizes after its formation upon dimerization to the closed shell system **1**.^{1–3} So far, only a limited number of monomeric closed shell derivatives, namely the parent hydroazafullerene HC₅₉N and RC₅₉N (R = Ph₂CH) described by Wudl and co-workers,^{4,5} as well the alkoxides ROC₅₉N and ROC₆₉N (R = CH₂CH₂OMe) reported by our group,² are known. These compounds are formed either during the synthesis of the heterofullerenes themselves as by-products or starting from the dimer **1** by trapping the homolysis product C₅₉N, for example, with Ph₂CH₂ in a radical substitution sequence. Here we report on an easy method for the synthesis of arylated mono adducts of C₅₉N in high yields by the thermal treatment of the dimer (C₅₉N)₂ **1** with aromatics in the presence of acid and oxygen.

Refluxing a solution of 25 mg of **1** in 30 ml of a 5 : 3 mixture of 1,2-dichlorobenzene (ODCB) and the corresponding aromatic with 50 equivs. of toluene-*p*-sulfonic acid in the presence of air for about 2–5 h results in almost quantitative conversion to the heterofullerene derivatives **2–4** (Scheme 1). After chromatographic purification (silica gel; toluene) the mono-adducts **2–4** were obtained in 78–90% isolated yield. Compounds **2** and **3** are the *para*-substitution products of anisole and toluene, whereas **4** is a mixture of different substitution products of 1-chloronaphthalene. We did not observe arylations with

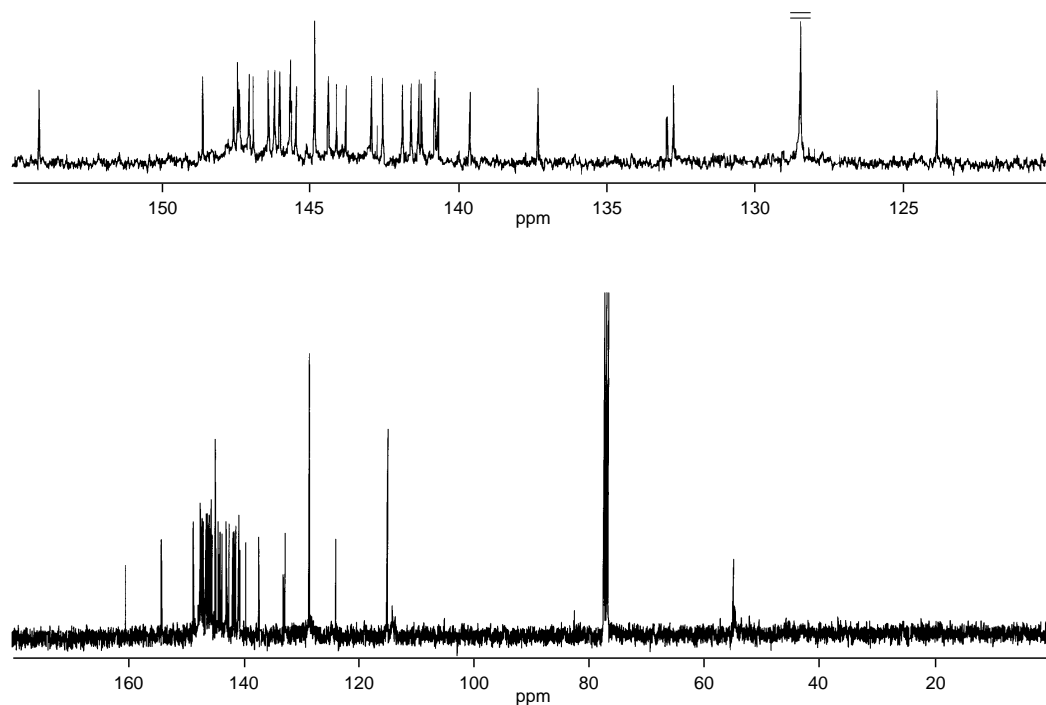
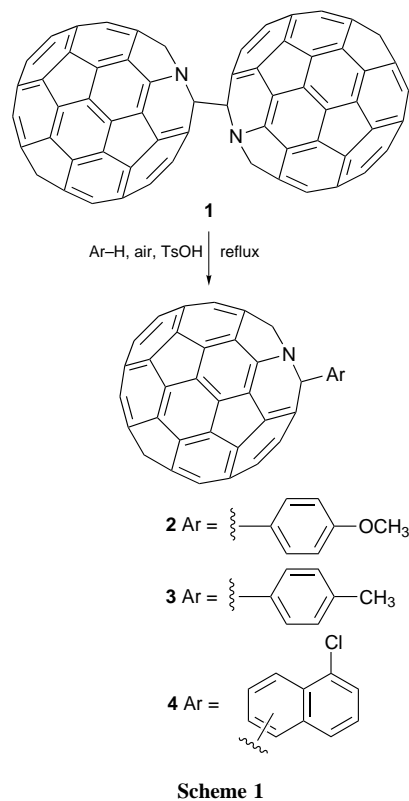
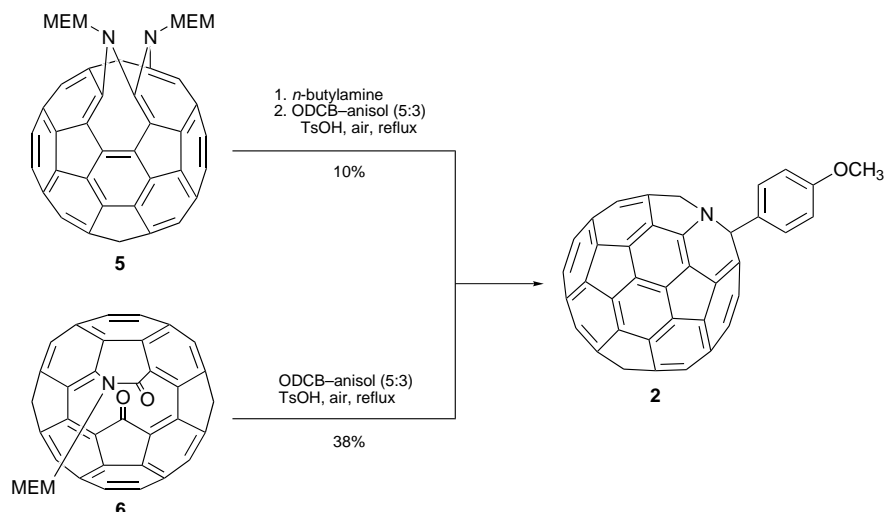


Fig. 1 ¹³C NMR (100.5 MHz, CS₂, 20% CDCl₃) spectrum for **2**, (top: expanded 120–155 ppm region)



Scheme 2

deactivated aromatics, which allows use of ODCB as solvent. In the absence of an acid or oxygen these derivatizations do not take place. The arylation with *N,N*-dimethylaniline failed. This is presumably due to the protonation of the Me_2N group causing deactivation towards electrophilic substitution.

The monoadducts **2–4** were characterized by ^1H NMR, ^{13}C NMR, UV–VIS and FTIR spectroscopy as well as by mass spectrometry.[†] The ^1H NMR spectrum of **2**, for example, shows the expected ddd-pattern of an AA'BB'-spin system for a *para*-substituted aromatic ring. The protons of the methoxy group resonate at δ 4.03. The ^{13}C NMR spectrum of **2** (Fig. 1) clearly proves C_s symmetry showing the 30 expected fullerene resonances in the sp^2 region between δ 155 and 123. The five different C-atoms of the anisyl addend resonate at δ 160.36, 132.94, 128.47, 115.01 and 54.93. The peak at δ 82.33 is due to the resonance of the sp^3 carbon of the fullerene skeleton, which is a typical value for a corresponding C atom in RC_{59}N .⁶ The UV–VIS spectra of **2–4** displaying the most intensive absorptions[†] at *ca.* 260, 320 and 440 nm are basically identical to that of **1**. All three compounds are green in solution. The FTIR spectra[†] of **2–4** show the typical characteristics for fullerene derivatives (monoadducts), especially the absorptions in the fingerprint region between 480 and 590 cm^{-1} with the strongest peak at about 523 cm^{-1} . MALDI-TOF mass spectrometry shows the M^+ peak of each compound together with a strong fragmentation peak at m/z 722 for C_{59}N^+ .

We assume that the mechanism of this reaction is an electrophilic aromatic substitution (S_{EAr}). The electrophile is presumably C_{59}N^+ , which might be formed *via* thermal homolysis of **1** and subsequent oxidation with O_2 . The reaction times depend on the nature of the aromatic reagent used. For example, the reaction of **1** with toluene took almost 5 h, whereas quantitative conversion with anisole was achieved within 2 h, which is in line with the lower S_{EAr} activity of toluene. The role of the acid is not clear. It is possible that it is needed to trap the reduced oxygen species.

It is important to mention that arylated adducts like **2** can also be obtained starting directly from the precursor molecules **5** and **6**, which are usually used for the synthesis of the heterofullerene dimer **1** (Scheme 2). Although the yields are considerably lower than those of the corresponding conversions using isolated **1**, one separation step can be avoided. However, the yields can be increased upon raising the reaction temperature. The direct treatment of **5** in 1-chloronaphthalene at 220 °C leads to the formation of **4** in 46% isolated yield.

Investigations on the chemical behaviour as well as on the electronic and photophysical properties of the stable arylated heterofullerene derivatives like **2–4** are currently underway.

We thank the DFG for financial support.

Notes and References

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[†] Selected spectroscopic data of the newly synthesised compounds **2–4**. **2**: FTIR: $\nu(\text{KBr})/\text{cm}^{-1}$ 2995, 2945, 2924, 2900, 2828, 1507, 1421, 1250, 1175, 1032, 966, 899, 840, 822, 718, 638, 587, 555, 523 and 482; UV–VIS $\lambda_{\text{max}}(\text{cyclohexane})/\text{nm}$ 257, 323, 444, 591, 723 and 789; $\delta_{\text{H}}(400 \text{ MHz}, \text{CS}_2-20\% \text{ CDCl}_3)$ 8.72 (ddd, J_{AB} 9.02, $J_{\text{AB}'}$ 3.10, $J_{\text{AA}'}$ 2.75, 1 H), 7.35 (ddd, J_{AB} 9.02, $J_{\text{AB}'}$ 3.10, $J_{\text{AA}'}$ 2.75, 1 H) and 4.03 (s, 3 H); $\delta_{\text{C}}(100.5 \text{ MHz}, \text{CS}_2-20\% \text{ CDCl}_3)$ 160.36 (C–OMe, 1C), 154.10 (2C), 148.61 (2C), 147.58 (1C), 147.44 (2C), 147.38 (2C), 147.06 (2C), 146.91 (2C), 146.41 (2C), 146.19 (2C), 146.02 (2C), 145.66 (2C), 145.63 (1C), 145.46 (2C), 144.83 (4C), 144.37 (2C), 144.11 (2C), 143.79 (2C), 142.93 (2C), 142.55 (2C), 141.89 (2C), 141.60 (2C), 141.34 (2C), 141.24 (2C), 140.80 (2C), 140.68 (2C), 139.60 (2C), 137.31 (2C), 132.94 [C–(CH)₂COMe, 1C], 132.72 (2C), 128.47 (C–CHCOMe, 2C), 123.89 (2C), 115.01 (C–COMe, 2C), 82.33 (1C) and 54.93 (Me); MALDI-MS m/z 828 (M^+), 814 ($\text{M}^+ - \text{Me}$) and 722 (C_{59}N^+). **3**: FTIR: $\nu(\text{KBr})/\text{cm}^{-1}$ 2919, 2845, 1736, 1629, 1509, 1422, 1374, 1344, 1316, 1262, 1236, 1186, 1095, 1020, 968, 901, 844, 803, 774, 719, 707, 679, 554, 525, 495, 483, 438, 428 and 409; UV–VIS $\lambda_{\text{max}}(\text{cyclohexane})/\text{nm}$ 263, 323, 440, 588, 722 and 790; $\delta_{\text{H}}(400 \text{ MHz}, \text{CS}_2-20\% \text{ CDCl}_3)$ 8.70 (ddd, not completely resolved, J_{AB} 7.77, 1 H), 7.67 (ddd, not completely resolved, J_{AB} 7.77, 1 H) and 2.66 (s, 3 H); $\delta_{\text{C}}(100.5 \text{ MHz}, \text{CS}_2-20\% \text{ CDCl}_3)$ 154.19 (2C), 148.69 (2C), 147.59 (1C), 147.42 (2C), 147.39 (2C), 147.08 (2C), 147.01 (2C), 146.41 (2C), 146.21 (2C), 146.03 (2C), 145.67 (2C), 145.65 (1C), 145.46 (2C), 144.84 (4C), 144.39 (2C), 144.11 (2C), 143.80 (2C), 142.95 (2C), 142.56 (2C), 141.90 (2C), 141.62 (2C), 141.34 (2C), 141.25 (2C), 140.80 (2C), 140.69 (2C), 139.61 (2C), 139.22 (q, 1C), 138.02 (q, 1C), 137.34 (2C), 132.75 (2C), 130.42 (C–CMe, 2C), 127.07 (C–CHCMe, 2C), 123.94 (2C), 82.60 (1C) and 21.48 (Me); MALDI-MS m/z 813 (M^+) and 722 (C_{59}N^+). **4**: FTIR: $\nu(\text{KBr})/\text{cm}^{-1}$ 2962, 2923, 2854, 1635, 1508, 1420, 1375, 1318, 1261, 1092, 1028, 800, 747, 722, 524 and 472; UV–VIS $\lambda_{\text{max}}(\text{cyclohexane})/\text{nm}$ 256, 320, 436, 580, 711 and 793; $\delta_{\text{H}}(400 \text{ MHz}, \text{CS}_2-20\% \text{ CDCl}_3)$ several multiplets between δ 7.0 and 10.5; $\delta_{\text{C}}(100.5 \text{ MHz}, \text{CS}_2-20\% \text{ CDCl}_3)$ 154.23, 148.34, 147.66, 147.53, 147.41, 147.27, 147.15, 146.73, 146.48, 146.38, 146.27, 146.24, 146.14, 145.74, 145.54, 144.96, 144.43, 144.34, 144.22, 143.79, 143.07, 142.81, 142.08, 141.86, 141.32, 140.96, 140.80, 139.80, 137.39, 137.38, 136.99, 133.34, 133.00, 129.20, 128.76, 128.05, 127.61, 127.45, 126.97, 126.50, 126.30, 125.75, 125.25, 124.82, 124.02 and 122.82; MALDI-MS m/z 884 (M^+) and 722 (C_{59}N^+).

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Received in Cambridge UK, 27th October 1997; 7/07704A