A new route to nitrogen heterofullerenes and the first synthesis of $(C_{69}N)_2$

Berthold Nuber and Andreas Hirsch*

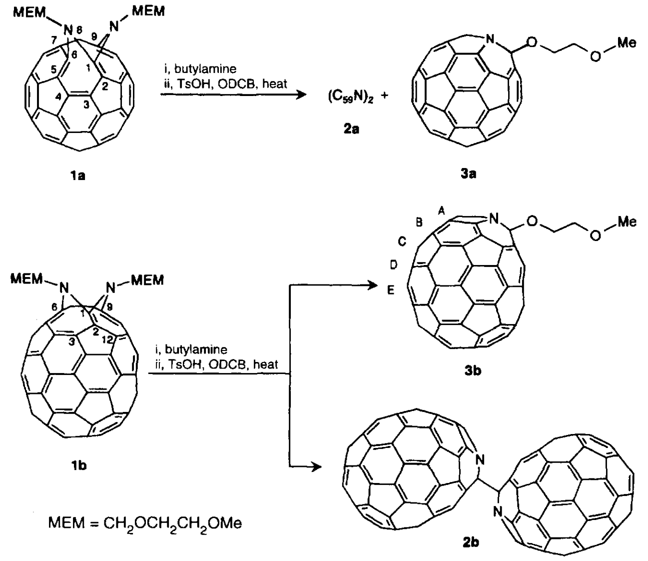
Institut für Organische Chemie, Henkestrasse 42, 91054 Erlangen, Germany

Heating butylamino adducts of diazabis-(1,6);(1,9)-homofullerenes bearing MEM-protected imino bridges with toluene-*p*-sulfonic acid provides a new route to $(C_{59}N)_2$ in macroscopic amounts and also provides, for the first time, the synthesis and isolation of $(C_{69}N)_2$ and the heterofullerene adducts $RC_{59}N$ and $RC_{69}N$.

We reported recently the mass spectrometric detection of the nitrogen heterofullerenes $C_{59}N^+$ and $C_{69}N^+$, formed by fragmentation of regioselectively synthesized iminofullerene derivatives.[1] At about the same time Mattay *et al.*[2] detected $C_{59}NH^+$ and $C_{59}NH_2^+$ by mass spectroscopy which were generated from 1,2-C_{60}NH using desorptive-chemical-ionization. Hummelen *et al.*[3] elaborated the first synthesis of the heterofullerene $C_{59}N$ in dimer form $(C_{59}N)_2$ from a cluster opened ketolactame precursor. Based on our initial investigations on the fragmentation of iminofullerenes to heterofullerenes[1] we now present a new macroscopic route to $(C_{59}N)_2$ and the synthesis and isolation of $(C_{69}N)_2$ and the heterofullerene adducts $RC_{59}N$ and $RC_{69}N$ [R = $O(CH_2)_2OMe$].

The synthesis of the heterofullerenes **2** and **3** (Scheme 1) using diazabis-(1,6);(1,9)-homofullerenes **1** as starting materials was achieved *via* their butylamine monoadducts, which we described earlier.[1] Formation of **2** and **3** was found to occur only if the substituents of the imino bridges can be easily removed by acids. For example, heterofullerenes were not obtained using the CH_2CO_2Me analogoue[4] of **1a** as starting material. This implies that during heterofullerene formation, which is accompanied by the elimination of one C-atom of the fullerene cage (most likely C-1) as an isonitrile or carbodiimide species, unprotected imino bridges are required. Hence, we choose the MEM protecting group as side-chains on the imino bridges. Treatment of **1a** with butylamine and DBU in toluene at room temperature led to the formation of the corresponding green aminofullerides, which mostly precipitate under these conditions. After removal of the toluene, the residue was dissolved in 1,2-dichlorobenzene and heated with 20 equiv. of toluene-*p*-sulfonic acid under reflux for 8 min to give $(C_{59}N)_2$ **2a** and the more polar **3a**, which were separated by flash-chromatography on silica gel with toluene as eluent. $(C_{69}N)_2$ **2b** and adduct **3b** were obtained in the same way using **1b** as educt.† The yields of **2a** and **2b** were 12–15% and those of **3a** and **3b** were *ca.* 10%. The major products of these reactions are insoluble materials, whose mass spectra essentially show peaks of free heterofullerene clusters, *e.g.* at *m/z* 722 ($C_{59}N^+$). Presumably, derivatives **3** are formed by trapping of the expected but unstable[3] $C_{59}N^+$ intermediates with the acetal cleavage product $HO(CH_2)_2OMe$.

The spectroscopic and analytical data of **2a** are identical to those reported by Hummelen *et al.*,[3] which implies that the dimer $(C_{59}N)_2$ was obtained, although, using several MS-techniques (EI, FD, FAB, MALDI) no peak for the dimer (*m/z* 1445) was observed but that for the $C_{59}N$-cluster (*m/z* 722) was exclusively observed, Fig. 1(*a*). Similarly, in the mass spectra of **2b**, Fig. 2(*a*), only the peak for $C_{69}N$ (*m/z* 842) was observed.‡ Given the reasonable assumption that $C_{69}N$ behaves the same way as $C_{59}N$ the dimeric structure **2b** in Scheme 1 is most likely for this heterofullerene. The UV–VIS spectrum‡ of **2b**, Fig. 2(*b*), resembles some of the features of C_{70} and looks very



Scheme 1

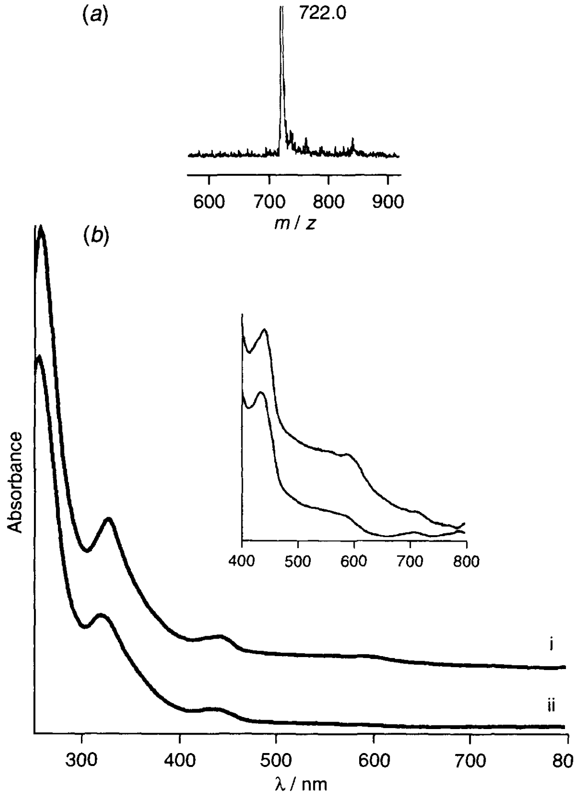


Fig. 1(*a*): MALDI-TOF mass spectrum of $(C_{59}N)_2$ **2a**. (*b*) UV–VIS spectra (cyclohexane) of **2a** (i) and **3a** (ii). The inset shows the expanded 400–800 nm regions of **2a** (top) and **2b** (bottom).

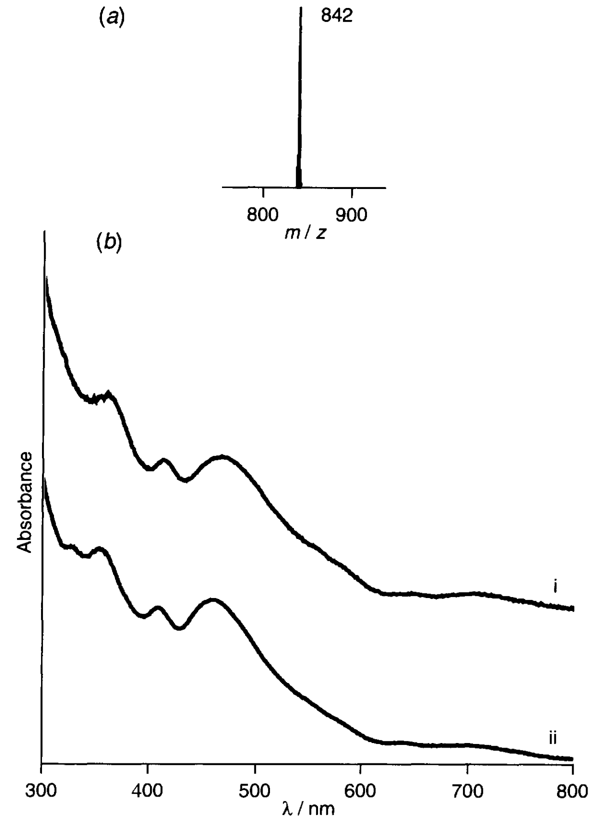


Fig. 2(*a*) EI mass spectrum of $(C_{69}N)_2$ **2b**. (*b*) UV–VIS spectra (toluene) of **2b** (i) and **3b** (ii) (cyclohexane).

similar to a typical spectrum of a 1,2-dihydro[70]fullerene[5,6] with the characteristic three absorptions between 300 and 500 nm. The widths and relative intensities of these peaks strongly depend on the solvent. No hydrogens other than that of solvent impurities (blank spectrum) are detectable in the ^{1}H NMR spectrum of **2b**. The solubility of **2b** in solvents like CS_2 and chloroform is rather low and hence no sufficient ^{13}C NMR spectral data of **2b** could be obtained.

The UV–VIS spectra‡ of the side products **3** are almost identical to those of the parent analogues **2**, Figs. 1(*b*), 2(*b*). The ^{13}C NMR spectra of **3** clearly prove C_s-symmetry with 31 signals for **3a** and 35 signals for **3b** in the corresponding sp^2-fullerene regions.‡ In addition to the expected three signals for the sp^3-C-atoms of the side-chains both spectra exhibit an additional signal at δ 90.03 for **3a** and at δ 96.42 for **3b** respectively, which are due to the sp^3-carbon atoms of the heterofullerene clusters themselves. The ^{1}H NMR spectra‡ of **3a** and **3b** are very similar. In each spectrum there are two multiplets for the two methylene and one singlet for the methyl groups with the integration ratio of 2 : 2 : 3. Compounds **3** are not stable and slowly decompose to give insoluble products, which show carbonyl vibrations in the IR spectra. In the EI-MS of **3** there were peaks at *m*/*z* 722 and 842, respectively, which are due to the parent heterofullerene clusters. This reveals a pronounced tendency of **3** to fragment. In the MALDI-MS spectrum of **3a** in addition to the peak of the $C_{59}N^+$ cluster a strong signal at *m*/*z* 738 was observed due to the fragment $NC_{59}O^+$.

We thank the Hoechst AG, the BMBF and the Otto-Röhm-Gedächtnisstiftung for financial support.

Footnotes

† The (1,6);(1,9)-isomer **1b** was synthesized *via* a two-fold reaction of C_{70} with MEM-N_3 in 1,2-dichlorobenzene at 120 °C. In contrast to C_{60}, C_{70} has distinguishable reactive sites which can lead to other isomers. Thus for example the C_s-symmetric isomer **1c** with a (2,3);(2,12)-addition pattern was formed as a side product, the **1b** : **1c** ratio being 4 : 1. It can be expected, that using **1c** as precursor a carbon in position B will be substituted by the nitrogen atom. Hence a mixture of **1b** and **1c** should react with three isomeric heterofullerenes dimers with an AA, AB and BB pattern. Analysis of the pre-purified mixture of $(C_{69}N)_2$ by HPLC (buckyclutcher, toluene : heptane = 9 : 1) revealed three fractions with increasing polarity in a ratio *ca.* 3 : 1 : 16. The largest, most polar fraction **2b** was isolated by preparative HPLC, the others were analysed with respect to their UV–VIS spectra by HPLC diode array detector. The UV–VIS spectra of the other two fractions are almost the same as that of **2b**, Fig. 2(*b*). Along with **3b** another stereoisomeric monoadduct **3c** with C_s-symmetry was formed in a small amount (**3b** : **3c** = 7 : 1).

‡ *Selected spectroscopic data* of the newly synthesised compounds **1a,b,2b,3a,b**. For **1a**: ^{1}H NMR (400 MHz, CS_2–20% $CDCl_3$) δ 5.54 (1 H, d, *J* 9.5 Hz), 5.40 (1 H, d, *J* 9.5 Hz), 4.16 (1 H, dt, J_A 11.1, J_B 4.6 Hz), 3.99 (1 H, dt, J_A 11.1, J_B 4.6 Hz), 3.69 (2 H, t, *J* 4.6 Hz) and 3.43 (3 H, s); ^{13}C NMR (100.5 MHz), CS_2–20% $CDCl_3$) δ 158.59, 147.30, 146.68, 145.18, 145.06, 144.65, 144.53, 144.29, 14.23, 143.89, 143.80, 143.67, 143.45, 143.27, 143.14, 142.48, 142.06, 141.53, 141.38, 140.00, 139.30, 139.14, 138.84, 137.95, 136.30, 135.04, 134.33, 132.80, 132.50, 130.09, 83.43, 71.87, 68.16 and 58.68; UV–VIS λ_{max}/nm (cyclohexane) 213, 259, 327, 432, 538 and 701; FT-IR (KBr) ν/cm^{-1} 2921, 1735, 1677, 1593, 1453, 1360, 1263, 1198, 1101, 846, 797, 760, 615, 557, 473, 464, 456, 447, 428, 422, 415 and 408, 403; FAB-MS *m*/*z* 927 (M^+), 852 [M^+–$O(CH_2)_2OMe$], 750 (M^+–2MEM) and 720 (C_{60}^+). For **1b**: ^{1}H NMR (400 MHz, CS_2–20% $CDCl_3$) δ 5.54 (1 H, d, *J* 9.5 Hz), 5.41 (1 H, d, *J* 9.4 Hz), 4.25 (1 H, dt, J_A 10.9, J_B 4.8 Hz), 4.08 (1 H, dt, J_A 10.9, J_B 4.8 Hz), 3.74 (2 H, t, *J* 4.7 Hz) and 3.46 (3 H, s); ^{13}C NMR (100.5 MHz, CS_2–20% $CDCl_3$) δ 152.22, 150.44, 150.36, 148.78, 148.52, 148.17, 147.93, 147.74, 147.05, 146.76, 146.19, 145.77, 145.34, 145.25, 144.49, 144.46, 144.08, 143.97, 143.91, 142.61, 140.69, 138.86, 137.28, 136.27, 135.83, 134.13, 132.88, 132.32, 131.43, 129.20, 128.44, 123.53, 83.81, 71.84, 68.25 and 58.58; UV–VIS λ_{max}/nm (cyclohexane) 215, 236, 256, 325, 392, 417, 459, 530, 666 and 711; FT-IR (KBr) ν/cm^{-1} 2918, 2872, 1672, 1567, 1452, 1429, 1347, 1255, 1219, 1198, 1102, 1028, 847, 794, 752, 737, 712, 670, 644, 635, 570, 559, 542, 528, 516, 502, 451, 426 and 411; FAB-MS, *m*/*z* 1047 (M^+), 972 [M^+–$O(CH_2)_2OMe$], 884 [M^+–$O(CH_2)_2OMe$–MEM] and 840 (C_{70}^+). For **2b**: UV–VIS λ_{max}/nm (cyclohexane) 230, 280, 354, 377, 406, 455, 639 and 679; FT-IR (KBr) ν/cm^{-1} 1511, 1429, 1262, 907, 823, 795, 672, 631, 578, 568, 559, 535, 457, 450 and 404; EI-MS *m*/*z* 842 ($C_{69}N$). For **3a**: UV–VIS λ_{max}/nm (cyclohexane) 212, 256, 321, 436, 582, 710 and 789; ^{1}H NMR (400 MHz, CS_2–20% $CDCl_3$) δ 4.93 (2 H, m), 3.97 (2 H, m) and 3.51 (3 H, s); ^{13}C NMR (100.5 MHz, CS_2–20% $CDCl_3$) δ 153.75, 148.07, 147.41, 147.30, 147.16, 147.10, 146.33, 146.28, 145.99, 145.75, 145.57, 145.48, 145.09, 144.95, 144.76, 144.65, 144.49, 144.05, 143.67, 143.01, 142.61, 141.90, 141.68, 141.27, 140.87, 140.74, 140.63, 139.74, 137.31, 133.02, 123.37, 90.03, 70.08, 66.44 and 58.78; MALDI-MS *m*/*z* 738 ($C_{59}NO^+$) and 722 ($C_{59}N^+$). For **3b**: UV–VIS λ_{max}/nm (cyclohexane) 228, 279, 328, 355, 409, 461, 640 and 699; ^{1}H NMR (400 MHz, CS_2–20% $CDCl_3$) δ 4.60 (2 H, m), 3.75 (2 H, m) and 3.40 (3 H, s); ^{13}C NMR (100.5 MHz, CS_2–20% $CDCl_3$) δ 152.78, 151.38, 151.30, 151.03, 150.37, 149.84, 149.66, 149.53, 149.02, 148.51, 148.23, 147.80, 146.83, 146.61, 146.32, 145.84, 145.70, 145.15, 143.87, 143.30, 142.70, 141.99, 141.86, 141.13, 140.82, 140.51, 140.34, 139.03, 136.69, 134.99, 132.54, 131.57, 131.44, 129.44, 121.27, 96.42, 69.82, 66.11 and 58.68; FT-IR (KBr) ν/cm^{-1} 2952, 2922, 1660, 1520, 1429, 1225, 1158, 1073, 1022, 795, 733, 671, 639, 631, 605, 578, 569, 559, 535, 451, 440, 417 and 404; EI-MS *m*/*z* 722 ($C_{69}N^-$).

References

1 I. Lamparth, B. Nuber, G. Schick, A. Skiebe, T. Grösser and A. Hirsch, *Angew. Chem.* 1995, **107**, 2473; *Angew. Chem., Int. Ed. Engl.*, 1995, **35**, 2257.

2 J. Averdung, H. Luftmann, I. Schlachter and J. Mattay, *Tetrahedron*, 1995, **51**, 6977.

3 J. C. Hummelen and F. Wudl, *Science*, 1995, **269**, 1554.

4 T. Grösser, M. Prato, V. Lucchini, A. Hirsch and F. Wudl, *Angew. Chem.*, 1995, **107**, 1462; *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1341.

5 A. Hirsch, T. Grösser, A. Skiebe and A. Soi, *Chem. Ber.*, 1993, **126**, 1061.

6 B. Nuber and A. Hirsch, *Full. Sci. Tech.*, 1996, in the press.

Received, 1st March 1996; Com. 6/01473I