Reaction of [60]Fullerene with Morpholine and Piperidine: Preferred 1,4-Additions and Fullerene Dimer Formation

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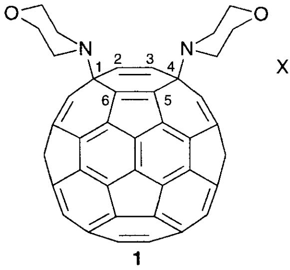
Reactions of an excess of secondary amines with benzene solutions of [60]fullerene in the presence of oxygen lead to dehydrogenated bisadducts and tetraadduct epoxides with a defined 1,4-addition pattern of the amino groups as well as to the first example of an aminated fullerene dimer.

Additions of primary and secondary amines to [60]fullerene are among the earliest reactions that have been observed in fullerene chemistry.[1,2] Polyaminofullerenes, for example, were obtained by the treatment of [60]fullerene with neat propylamine, whereupon, in an initial fast process green solutions are formed, which eventually turn chestnut-brown.[1] Carefully monitoring these reactions with EPR and UV–VIS–NIR spectroscopy showed, that the first step is a single electron transfer from the amine to C_{60} to give the $C_{60}{}^{\cdot -}$ radical anion.[3] The next step is radical recombination and the formation of zwitterions, which in principle can stabilise by proton transfer from the amine to C_{60} or by oxidation (air) followed by deprotonation and radical recombination. Although reactions of [60]fullerene with amines, either in solution or with the neat amine proceed very easily, only few cases of the isolation of defined aminofullerenes have been reported because, very often, complex mixtures of aminoadducts are obtained. It is important to note that especially the expected hydroamination products[4] do not form in most cases, where oxygen was not strictly excluded. Instead, for example by the reaction of C_{60} with secondary diamines like piperazine, dehydrogenated 1,2-diaminocycloadducts have been isolated.[5,6] In this paper we report on the reaction of [60]fullerene with an excess of morpholine or piperidine in benzene in the presence of oxygen and the exclusive isolation of dehydrogenated aminoadducts with a preferred 1,4-addition pattern as well as on the first aminated fullerene dimer with a single inter-fullerene connection.

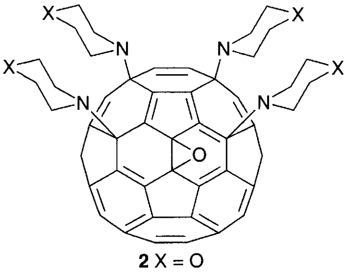
The treatment of an air-saturated benzene solution of C_{60} with a 40-fold excess of morpholine for one week led to a colour change from purple to brown and to the formation of a dark precipitate. After this time 70% of C_{60} was consumed (HPLC). Next to the black 1,4-dimorpholino-1,4-dihydro[60]fullerene **1** and the golden yellow 1,2-oxo-4,11,15,30-tetramorpholino-1,2,4,11,15,30-hexahydro[60]fullerene **2**, which were isolated by preparative HPLC [silica gel; toluene–ethyl acetate (60 : 40)] in 8.5 and 9.1% yield, respectively, the soluble fraction contained a variety of other components in trace amounts. The dark precipitate, which was formed in 50% yield as the major reaction product is the dimer bis-[(4,4′-dimorpholino)-1,4-dihydro[60]fullerenyl] **3**, which is the first isolated and characterized representative of this structure type.[7]

The ^{1}H NMR spectrum† of **1** shows only two distinct quartets for the two different CH_2 groups of the morpholine addends at δ 3.98 and 3.66 and the ^{13}C NMR spectrum† exhibits 32 signals for the fullerene-C atoms, with four of half intensity and one at δ 73.54 for the sp^3-fullerene-C atoms carrying the morpholine addends, reflecting the C_s symmetry of **1**. Hence, the presence of a 1,2-addition product with C_{2v} symmetry can be excluded. Four multiplets for the four different CH_2 groups at δ 3.84, 3.78, 3.30 and 3.16 are observed in the ^{1}H NMR spectrum† of **2**. The C_s-symmetric structure of **2** can also be deduced from its ^{13}C NMR spectrum,† which shows 32 lines (four of half intensity). In the sp^3 region the resonances at δ 76.61 (C–O), 71.80 (C–O) both of half intensity and at δ 75.90 (C–N), 72.21 (C–N) are attributed to the fullerene C-atoms carrying the oxygen and morpholine addends. The UV–VIS spectrum† of **1** is similar to those of typical 1,2-dihydrofullerene derivatives,[8] however, with the significant difference, that in contrast to the latter no sharp absorption at 430 nm but at broad peak at 443 nm is observed. The UV–VIS spectrum† of **2** is similar to that of $C_{60}Cl_6$,[9] having the same addition pattern. The FTIR spectra† of **1** and **2** differ characteristically in the region of the fullerene core vibrations between 525 and 580 cm^{-1}, which in analogy to methanofullerenes[10] is a significant fingerprint for the different degree of addition. In contrast to **1**, the peak of **2** at 527 cm^{-1} is much less intense compared to the other vibrations in this area, reflecting a larger deviation of the vibrational properties from that of free [60]fullerene. The reaction of [60]fullerene with piperidine leads to analogous results. For example, the golden-yellow adduct **4**,† which is isostructural to **2** was isolated as the major product of the soluble fraction.

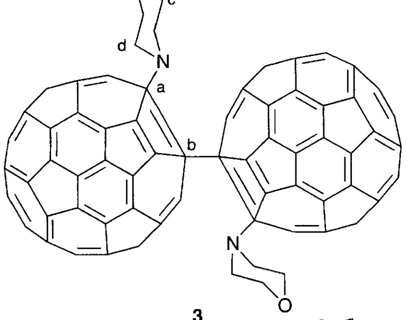
The dimer **3** is insoluble in most organic solvents and only slightly soluble in *o*-dichlorobenzene. Its structure has been determined using solid state ^{13}C NMR techniques,† cross polarisation–magic angle spinning (CP–MAS), together with selective population inversion (CP–MAS–SPI) or non quarternary suppression (CP–MAS–NQS). Three of the four



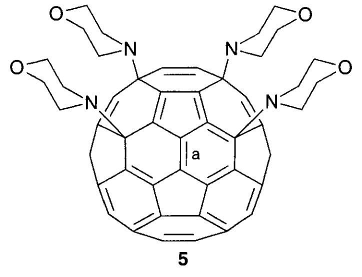
1



2 X = O
4 X = CH_2



3



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expected signals of the four different sp^3 atoms in **3** at δ 74.28, 66.99 and 49.37 can be resolved by standard CP–MAS. Using the CP–MAS–SPI-technique, where secondary C atoms give rise to emissions and quarternary C atoms to absorptions, four different signals can indeed be resolved. The emissions at δ 66.99 and 49.37 are due to C-c and C-d of the magnetically identical morpholine addends and the absorptions at δ 74.28 and 66.99 are due to the C-a and C-b of the fullerene core. In the CP–MAS–NQS spectra only the signals of the quarternary atoms C-a and C-b appear, which unambiguously proves their correct assignment. The sp^2-C atoms of **3** resonate as a broad group of signals centred at δ 145.15. The UV–VIS spectrum† (*o*-dichlorobenzene) and the FTIR spectrum† of **3** are almost identical to those of **1**, showing that 1,4-addition patterns are involved in each fullerene moiety of **3**.

The fact that only dehydrogenated products were isolates shows that initially formed intermediates like aminated fullerene carbanions $R_2NC_{60}^-$ or zwitterions $R_2HN^+C_{60}^-$ are oxidised by oxygen, presumably $^1O_2$, to form aminated radicals R_2NC_{60}·. Radical recombination can either be achieved by dimerisation or by further additions of morpholine moieties in a sequence of oxygen or fullerenyl radical promoted radical formation and recombination processes. The presence of radical processes is strongly supported by the fact that the same addition patterns involved in **1**, **2** and **4** have also been observed by in situ EPR investigations of additions of benzyl radicals[11] to C_{60}. Moreover, **2** and **4** are isostructural to $C_{60}Cl_6$[9] and $C_{60}Br_6$,[12] obtained by halogenation. In all of these cases, preferred successive 1,4-additions take place. This is mainly due to 1,2-additions eclipsing interactions between these sterically demanding addends would be larger[13] than the energy required for the introduction of double bonds in five-membered rings as a consequence of 1,4-additions. In adducts arising from subsequent 1,4-addition the number of 5–6 double bonds is minimised compared to other addition patterns, except 1,2-additions. PM3 calculations of **1** and **5**, which is the not isolated kinetically unstable precursor of **3** in addition reveal that the LUMO coefficients are significantly highest at the 4-positions relative to the addends already bound at the corresponding corannulene unit. Another driving force for this reaction pathway is the formation of resonance stabilised allyl radicals X_3C_{60}· and cyclopentadienyl radicals X_5C_{60}·.[11] Radical recombination, finally requires one 1,2-addition process to form a stable diamagnetic compound. In the case of **2** and **4** the formation of a less demanding epoxide bridge instead of sterically demanding 1,2-amino additions is involved to complete the addition sequence. The double bond *a* (1.35 Å) in **5** is by far the shortest and, therefore, the most reactive in the molecule (PM3). Hence, it is not surprising that **5** doesn't form as an isolable product but is easily converted to **2**. The diaminofullerene **1** is the first example of an isolated isomerically pure 1,4-dihydrofullerene derivative. The isolation of dimer **3** corroborates EPR experiments, where dimerisation of RC_{60}· radicals have been postulated.[7]

We thank the DFG, the BMFT and the Hoechst AG for financial support. We further are indebted to Dr Stefan Fiedler from the University of Tübingen for recording the solid state NMR spectra.

Received, 21st July 1995; Com. 5/04815J

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† *Selected spectroscopic* data for **1**: ^{1}H NMR (250 MHz, CS_2–20% $CDCl_3$, 25 °C) δ 3.98 (q), 3.66 (q); ^{13}C NMR (62.9 MHz, CS_2–20% $CDCl_3$, 25 °C) δ 150.74 (2 C), 149.50 (2 C), 148.59 (2 C), 147.29 (2 C), 146.97 (2 C), 146.86 (2 C), 146.79 (2 C), 146.63 (2 C), 146.45 (2 C), 146.13 (1 C), 145.58 (2 C), 145.32 (2 C), 144.26 (2 C), 144.18 (2 C), 144.11 (2 C), 144.03 (2 C), 143.62 (1 C), 143.48 (2 C), 143.35 (2 C), 143.17 (2 C), 143.13 (2 C), 142.96 (2 C), 142.94 (2 C), 142.91 (2 C), 142.47 (2 C), 142.23 (2 C), 142.04 (1 C), 141.06 (2 C), 140.35 (1 C), 139.70 (2 C), 138.20 (2 C), 73.54 (2 C–N), 67.17 (2 C), 50.48 (2 C); UV–VIS λ_{max}/nm (CH_2Cl_2) 257, 330 (sh), 443; FTIR ν/cm^{-1} (KBr) 2951, 2887, 2847, 21447, 1431, 1388, 1285, 1269, 1117, 1207, 1188, 1117, 1069, 1009, 878, 578, 561, 527.

For **2**: ^{1}H NMR (250 MHz, CD_2Cl_2, 25 °C) δ 3.84 (m), 3.78 (m), 3.30 (m), 3.16 (m); ^{13}C NMR (62.9 MHz, $C_2D_2Cl_4$, 25 °C) δ 151.46 (2 C), 149.55 (4 C), 149.37 (2 C), 149.30 (2 C), 148.00 (1 C), 147.92 (2 C), 147.64 (2 C), 147.31 (4 C), 147.25 (2 C), 147.19 (2 C), 147.13 (2 C), 147.03 (2 C), 146.52 (2 C), 146.35 (2 C), 145.48 (1 C), 145.36 (2 C), 144.86 (2 C), 144.47 (2 C), 144.31 (2 C), 144.08 (2 C), 143.87 (2 C), 143.70 (2 C), 143.34 (2 C), 143.14 (2 C), 141.87 (2 C), 140.59 (2 C), 76.61 (1 C–O), 75.90 (2 C–N), 72.21 (2 C–N), 71.80 (1 C–O), 67.59 (4 C), 67.49 (4 C), 51.62 (4 C), 51.22 (4 C); UV–VIS λ_{max}/nm (CH_2Cl_2) 257, 273 (sh), 301 (sh), 341 (sh), 362 (sh), 398 (sh); FTIR ν/cm^{-1} (KBr) 2953, 2922, 2851, 1450, 1391, 1288, 1269, 1117, 1066, 1011, 878, 860, 553, 538, 527; MS (FD) (M^+) 1081.

For **3**: ^{13}C NMR (CP–MAS, CP–MAS–SPI, CP–MAS–NQS, 25 °C) δ 144.15 (sp^2-C), 74.28 (C-1), 66.99 (C-2, C-3), 49.37 (C-4); UV–VIS λ_{max}/nm (ODCB) 444, 331; FTIR ν/cm^{-1} (KBr) 2953, 2916, 2848, 2820, 1447, 1431, 1286, 1269, 1184, 1114, 1070, 1009, 879, 849, 579, 569, 557, 527.

For **4**: ^{13}C NMR (100.6 MHz, CS_2–$CDCl_3$, 30 °C) δ 151.82 (2 C), 150.06 (2 C), 149.53 (2 C), 149.00 (2 C), 148.74 (2 C), 147.41 (4 C), 147.12 (2 C), 146.99 (2 C), 146.82 (2 C), 146.71 (2 C), 146.56 (4 C), 146.03 (2 C), 145.92 (2 C), 145.03 (3 C), 144.79 (2 C), 144.60 (2 C), 143.70 (2 C), 143.56 (2 C), 143.48 (2 C), 143.22 (2 C), 142.80 (1 C), 142.72 (2 C), 142.57 (2 C), 141.19 (2 C), 140.14 (2 C), 76.28 (1 C–O), 75.85 (2 C–N), 72.16 (2 C–N), 71.03 (1 C–O), 52.11 (4 C), 51.66 (4 C), 27.05 (8 C), 24.97 (2 C), 24.70 (2 C); MS (FAB) (M^-) 1072.

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