Pyrrole-embedded [60]fullerenes

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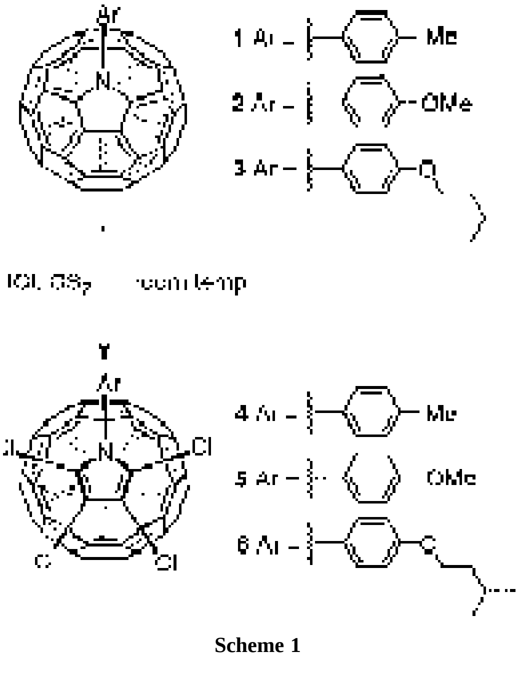
The treatment of the monoarylated azafullerenes $ArC_{59}N$ with iodine monochloride in carbon disulfide leads to the exclusive formation of the tetrachlorinated heterofullerenes $Cl_4ArC_{59}N$ which contain a pyrrole moiety in the fullerene cage.

Recently, we reported on the synthesis of arylated heterofullerenes $ArC_{59}N$.[1] These systems are suitable compounds for the investigation of the chemistry of azafullerenes, because they are stable and more soluble than the parent dimer $(C_{59}N)_2$.

Here, we report on the facile chlorination of azafullerenes $ArC_{59}N$ with ICl. The reaction of C_{60} with ICl was previously described by Birkett *et al.*[2] and leads to the quantitative formation of $C_{60}Cl_6$. This C_s symmetrical compound exhibits an addition pattern with five Cl atoms attached in 1,4 positions at the outer and one at the inner perimeter of a corannulene substructure, leaving a cyclopentadiene moiety within the fullerene framework. Consequently, the reaction with azafullerene derivatives $ArC_{59}N$ should yield the related tetrachlorinated species $Cl_4ArC_{59}N$ containing an integral pyrrole moiety decoupled from the conjugated π-system of the fullerene cage.

For the synthesis of the pyrrole-embedded fullerenes **4**–**6** a freshly prepared solution of 25 equiv. of ICl in CS_2 was added to a solution of 1 equiv. of the azafullerene derivatives **1**–**3** in CS_2 at room temperature (Scheme 1). This mixture was stirred for 10 min and then allowed to stand in the dark for three days for the decomposition of the excess ICl. Subsequently, the solvent and most of the iodine were removed *in vacuo*. After chromatography on silical gel (toluene) the chlorinated compounds **4**–**6** were isolated in 50–60% yield as orange powders (**6** had to be further purified by HPLC on a semipreparative Cosmosil column). The reaction can easily be monitored by HPLC using a Cosmosil column and toluene as eluent, since compounds **4**–**6** show a significantly longer retention time than the corresponding educts. Compounds **4** and **5** are only sparingly soluble in CS_2. This turned out to be a serious problem, as no ^{13}C NMR spectra of sufficient intensity could be obtained. Compound **6** however is soluble enough (about 3 mg ml^{-1} in CS_2) to obtain a well-resolved ^{13}C NMR spectrum corroborating the depicted structure.[‡] The spectrum shows 26 resolved of the 28 expected signals for the sp^2 C-atoms of the fullerene cage between δ 160 and 128. The eight different carbon atoms of the isopentoxyphenyl moiety resonate at δ 22.54, 25.15, 37.93, 66.25, 115.19, 126.35, 128.78 and 159.95. Because of the long relaxation times of the sp^3 C-atoms of the fullerene cage their signals do not show up using a delay time of 6 s. To detect these signals longer pulse delay times, *e.g.* 16 s, are required.[3] In order to avoid very long measurements, we decided to use undeuterated 1,2-dichlorobenzene as solvent making use of the solvent heteronuclear NOE.[4] The two expected sp^3 signals appear at δ 57.31 and 58.42[‡] In $C_{60}Cl_6$, the corresponding C-atoms resonate at δ 54.93 and 55.42.[2] The signal for Cl (Fig. 1) appears at δ 70.19. The ^1H NMR spectra of **4**–**6** resemble those of the educts **1**–**3**.[‡] All signals show an upfield shift which is stronger for those hydrogens closer to the fullerene cage. The resonances are centred at δ 2.52, 7.42 and 8.06 for **4**, 3.91, 7.16 and 8.11 for **5** and 1.01, 1.73, 1.87, 4.05, 7.05 and 8.06 for **6**. The UV–VIS spectrum of **6** is very similar to that of $C_{60}Cl_6$,[2] with the λ_{max} values[‡] located at 237, 283, 345, 394, 434, 475 and 518 nm. The FTIR spectrum of **6** displays intense bands[‡] for the C–Cl vibrations at 846 and 817 cm^{-1}. The FTIR and UV–VIS spectra of **4** and **5** are basically identical to those of **6**.[‡] In the mass spectra (FAB, MALDI-TOF, EI) of **4**–**6** no M^+ peak could be detected due to facile loss of the Cl addends.[5]

An AM1 calculation (SPARTAN 4.0) on **4** (Fig. 1) reveals a geometry of the integral pyrrole moiety which is very similar to



Scheme 1

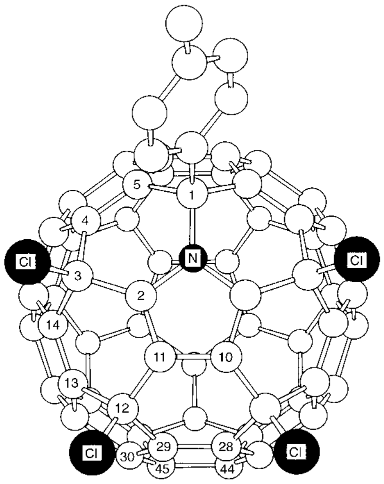


Fig. 1 AMl calculated structure of **4**. Selected bond lengths (pm): N–C2 140.8, C2–C11 140.7, C10–C11 143.4, C1–N 148.0, C2–C3 149.8, C11–C12 148.4, C1–C5 155.1, C4–C5 136.7, C3–C4 152.9, C3–C14 153.9, C13–C14 136.9, C12–C13 153.5, C12–C29 153.7, C28–C29 137.0, C29–C30 145.0, C30–C45 138.8, C44–C45 145.4.

the parent pyrrole. For example, the bond distances between C2–N, C2–C11 and C10–C11 are 140.8, 140.7 and 143.4 pm. Those of the parent compound are 139.2, 140.2 and 142.5 pm (AM1) or 137.0, 138.2 and 141.7 pm (exp.).[6] The pyrrole moiety is not completely planar; the dihedral angle between N–C2–C11–C10 is about 4°. The cage-centred HOMO of **4** has its coefficients exclusively on the [6,6]-bonds forming the equatorial belt of **4**, *e.g.* between C30 and C45. The shortest remaining double bonds are those located at the outer perimeter of the corannulene subunit. For example, the bond length between C4 and C5 is 136.7 pm. The highest Mulliken charges are also found at these C-atoms, whereas the charges at the C-atoms of the southern hemisphere are zero. These factors could be relevant for the regioselectivity of further addition reactions to systems like **4–6**.

The chlorine addends can be easily removed from the cage by treatment of **4–6** in 1,2-dichlorobenzene with an excess of PPh_3 at room temperature. The parent compounds **1**–**3** were obtained in good yield.[5,7]

Investigations on the chemistry of fulleropyrroles like **4–6**, and especially on their use as potential precursors for $C_{58}N_2$ derivatives formed by an azide addition/dechlorination sequence, are currently underway.

We thank the Deutsche Forschungsgemeinschaft (DFG) for financial support.

Notes and References

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‡ *Selected data* for **3**: ν(KBr)/cm^{-1} 2953, 2924, 2867, 1734, 1606, 1580, 1509, 1462, 1418, 1384, 1366, 1308, 1251, 1222, 1178, 1114, 1058, 1012, 838, 555 and 525; λ_{max}(cyclohexane)/nm 256, 315, 355 and 441; δ_H(400 MHz, CS_2–20% $CDCl_3$) 8.67 (ddd, J_{AB} 8.6, 2 H), 7.30 (ddd, J_{AB} 8.6, 2 H), 4.18 (t, J 6.35, 2 H), 1.95 (m, 1 H), 1.81 (m, 2 H) and 1.07 (d, J 6.8, 6 H); δ_C(100.5 MHz, CS_2–20% $CDCl_3$) 159.97 (C-OR, 1 C), 154.16 (2 C), 148.72 (2 C), 147.62 (1 C), 147.49 (2 C), 147.42 (2 C), 147.09 (2 C), 146.98 (2 C), 146.43 (2 C), 146.23 (2 C), 146.05 (2 C), 145.70 (2 C), 145.67 (1 C), 145.50 (2 C), 144.88 (4 C), 144.41 (2 C), 144.13 (2 C), 143.84 (2 C), 142.96 (2 C), 142.58 (2 C), 141.92 (2 C), 141.63 (2 C), 141.39 (2 C), 141.26 (2C), 140.82 (2 C), 140.72 (2 C), 139.64 (2 C), 137.35 (2 C), 132.75 (4 C), 128.47 (phenyl, 2 C), 123.94 (q, 1 C), 115.52 (phenyl, 2 C), 82.39 (q, 1 C), 66.35 (C-CH_2CHMe_2, 1 C), 38.03 (C-$CHMe_2$, 1 C), 25.22 (C-Me_2, 1 C) and 22.60 (Me, 2 C); m/z (EI) 885 (M^+) and 722 ($C_{59}N^+$).

For **4**: ν(KBr)/cm^{-1} 3027, 2919, 2854, 1735, 1626, 1511, 1462, 1443, 1420, 1377, 1341, 1316, 1265, 1239, 1189, 1104, 1073, 1054, 1021, 966, 945, 904, 845, 824, 779, 761, 709, 670, 625, 576, 563, 547, 513, 496, 452 and 434; λ_{max}(cyclohexane)/nm 239, 284, 337, 393, 433 and 470; δ_H(400 MHz, CS_2–20% $CDCl_3$) 8.06 (ddd, J_{AB} 8.3, 2 H), 7.42 (ddd, J_{AB} 8.3, 2 H) and 2.52 (s, 3 H).

For **5**: ν(KBr)/cm^{-1} 3000, 2953, 2927, 2901, 2833, 1640, 1606, 1511, 1461, 1439, 1420, 1340, 1302, 1257, 1181, 1103, 1073, 1033, 967, 945, 905, 846, 820, 779, 760, 709, 671, 649, 625, 577, 563, 546, 512, 454 and 433; λ_{max}(cyclohexane)/nm 239, 283, 337, 393, 435 and 477; δ_H(400 MHz, CS_2–20% $CDCl_3$) 8.11 (ddd, J_{AB} 8.8, 2 H), *ca.* 7.25 (ddd, covered by $CHCl_3$) and 3.91 (s, 3 H).

For **6**: ν(KBr)/cm^{-1} 2951, 2921, 2868, 2850, 1608, 1578, 1511, 1463, 1421, 1384, 1301, 1254, 1219, 1181, 1103, 1073, 1054, 1021, 967, 945, 905, 846, 817, 760, 709, 671, 624, 578, 563, 547, 512 and 434; λ_{max}(cyclohexane)/nm 237, 283, 345, 394, 434 and 475; δ_H(400 MHz, CS_2–20% $CDCl_3$) 8.06 (ddd, J_{AB} 8.8, 2 H), 7.05 (ddd, J_{AB} 8.8, 2 H), 4.05 (t, J 6.59, 2 H), 1.86 (m, 1 H), 1.72 (m, 2 H) and 1.01 (d, J 6.26, 6 H); δ_C(100.5 MHz, CS_2–20% $CDCl_3$) 160.06 (C-OR, 1 C), 150.10, 149.64, 149.27, 148.90, 148.78, 147.29, 147.24, 147.20, 147.05, 147.00, 146.85, 146.13, 146.00, 145.62, 145.01, 144.37, 144.29, 143.75, 143.67, 143.44, 143.18, 143.13, 140.68, 136.18, 129.04, 128.84 (phenyl, 2 C), 128.07, 126.41 (q, 1 C), 115.25 (phenyl, 2 C), 66.24 (C-CH_2-$CHMe_2$, 1 C), 37.88 (C-$CHMe_2$, 1 C), 25.10 (C-Me_2, 1 C) and 22.48 (Me, 2 C); δ_C(125.65 MHz, 1,2-dichlorobenzene–20% $CDCl_3$) 70.19 (q), 58.42 (C-Cl) and 57.31 (C-Cl).

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Received in Cambridge, UK, 27th April 1998; 8/03112F