X-Ray structure of 1′-(2-methoxyethoxymethyl)triazolinyl-[4′,5′ : 1,2]-1,2-dihydro[60]fullerene

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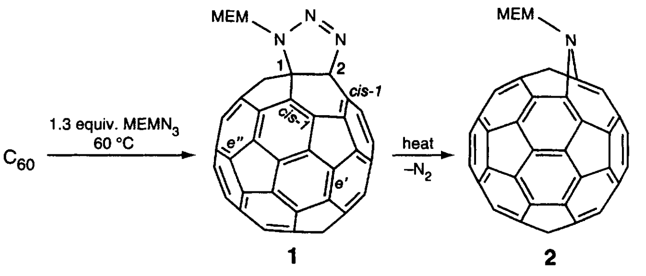
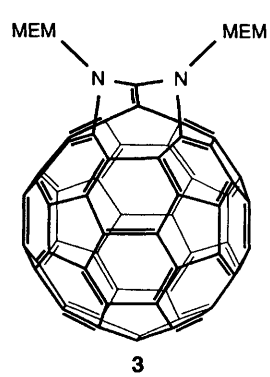
The X-ray structure of 1′-(2-methoxyethoxymethyl)-triazolinyl-[4′,5′ : 1,2]-1,2-dihydro[60]fullerene which is a key intermediate in the synthesis of nitrogen heterofullerenes is described.

We reported recently[1] that the regioselective formation of open [5,6]-bridged aza-1,6-homo[60]fullerenes as well as of diazabis-(1,6);(1,9)homo[60]fullerenes by the thermal reaction of [60]fullerene with alkyl azides proceeds *via* triazoline intermediates $C_{60}N_3R$ and $C_{60}(NR)(N_3R)$, respectively (Scheme 1). In the meantime, these types of nitrogen containing fullerene adducts have gained additional importance since it was discovered that both aza-1,6-homo[60]fullerene **2** and diazabis-(1,6); (1,9)homo[60]fullerene **3** containing the acid removable MEM group (MEM = methoxyethoxymethyl) can be converted into nitrogen heterofullerenes,[2,3] *e.g.* the dimer $(C_{59}N)_2$. Here we describe the synthesis, spectroscopic characterization† and X-ray crystal structure‡ of the key intermediate $C_{60}N_3MEM$ **1**.

The fullero triazoline **1** was obtained in 30% yield by stirring C_{60} with 1.3 equiv. of N_3MEM in 1,2-dichlorobenzene or 1-chloronaphthalene at 60 °C overnight (Scheme 1). Isolation of **1** was achieved by flash chromatography with toluene–ethyl acetate (9 : 1) on silica gel. Single crystals of **1**, suitable for X-ray analysis (Fig. 1), were grown in toluene. The compounds crystallizes without inclusion of solvent molecules in the monoclinic space group *P*2(1)/*c*. In the crystal **1** has C_1-symmetry. The average bond lengths are 1.450 Å for the [5,6]-bonds and 1.385 Å for the [6,6]-bonds excluding the



Scheme 1



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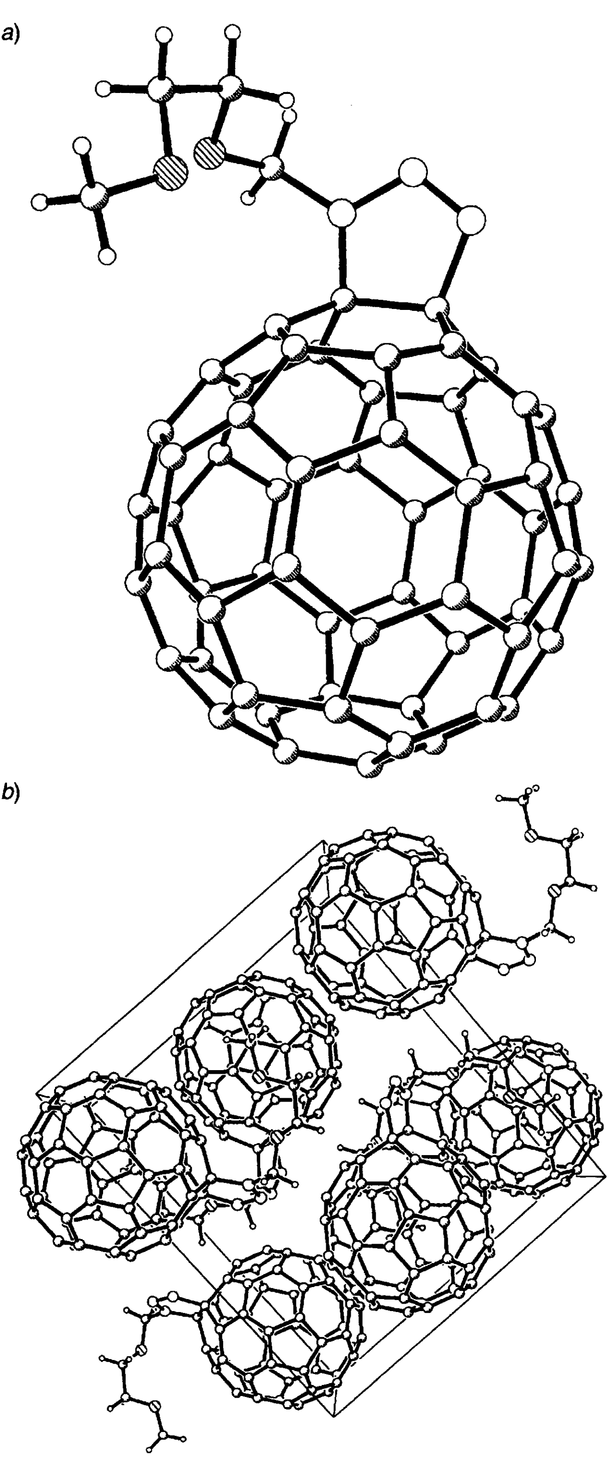

Fig. 1 (*a*) X-Ray crystal structure of **1** and (*b*) representation of the crystal packing in the unit cell

bridged [6,6]-bond between C-1 and C-2, which clearly shows that the [5]radialene-type structure[4] of the fullerene cage is preserved.

The [3+2]cycloaddition (Scheme 1) of the azide leads to the formation of a slightly elongated single bond in **1** between C-1 and C-2 with a bond length of 1.574 Å. Owing to the binding of the azide addend the fullerene cage in **1** becomes distorted relative to free C_{60}. The distortion of the fullerene cage is reflected, *e.g.* by the bond length deviations of the [6,6]-double bonds from the average value (1.385 Å) in **1**. The *cis-1*-bonds[5] with an average length of 1.362 Å are the significantly shortest [6,6]-double bonds within the molecule. The next longer are the *e′*- and *e″*-bonds with an average value of 1.383 Å. As a consequence, the diameters of the carbon cage perpendicular and parallel to the triazoline ring differ by 0.041 Å and the sphere is flattened along the axis perpendicular to the bridged double bond. A comparison of the X-ray structure of **1** with that of other monoadducts shows[6,7,8] that this particular distortion of the fullerene cage (*e.g.* short *cis-1*- and *e″*-bonds) is caused by the binding of the first addend and is not restricted to **1**. The cage distortion[6,7,8] in a 1,2-monoaddition adduct of C_{60} (1,2-dihydro[60]fullerene) is the reason for the regioselectivity of a second addition to a [6,6]-bond in the molecule.[8,9,10] In general, sterically demanding addends prefer to add to *e*-positions, whilst sterically non-demanding addends prefer to add to the *cis-1*- and *e*-positions.

The isolation of bis(triazolinyl)fullerenes and their conversion into the corresponding diazabishomo-[60]fullerenes with the two non adjacent imino bridges could be a key step in the synthesis of bisazafullerenes like $C_{58}N_2$, *via* known methods[2,3] used for the preparation of $C_{59}N$- or $C_{69}N$-heterofullerenes.

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Footnotes

† *Spectroscopic data* for **1**: ^1H NMR (400 MHz, CS_2–20% $CDCl_3$) δ 5.92 (2 H, s), 3.96 (2 H, t), 3.58 (2 H, t) and 3.32 (3 H, s); ^{13}C NMR (100.5 MHz, CS_2–20% $CDCl_3$) δ 147.29, 147.17, 146.00, 145.92, 145.72, 145.69, 145.64, 145.55, 145.16, 144.90, 144.85, 144.46, 144.04, 143.82, 143.75, 142.70, 142.55, 142.46, 142.39, 142.17, 141.91, 141.89, 141.72, 141.67, 141.50, 140.43, 139.95, 136.02, 135.62, 78.40, 77.78, 71.53, 67.59 and 58.73; UV–VIS λ_{max}/nm (cyclohexane) 214, 256, 315, 325 (sh), 425 and 461; FT-IR (KBr) ν/cm^{-1} 2948, 2915, 2863, 2328, 1735, 1584, 1551, 1503, 1461, 1425, 1364, 1344, 1327, 1290, 1273, 1238, 1214, 1187, 1093, 963, 845, 837, 820, 807, 762, 746, 730, 712, 683, 653, 624, 579, 568, 557, 551, 546, 529, 524, 505, 482, 469, 434, 424 and 413; FAB-MS *m*/*z* 853 (M^+) and 720 (C_{60}^+).

‡ *Crystal data* for **1**: M_r = 851.74; monoclinic; spacegroup $P2_1/c$; cell dimensions: a = 17.057(3), b = 14.108(3), c = 13.947(3) Å, β = 104.41(3)°; V = 3250.6(11) Å^3; $D_{calc.}$ = 1.740 mg m^{-3}; Z = 4; $F(000)$ = 1720; graphite monochromated Mo-Kα radiation (λ = 0.71073); T = 193(2) K. Data were collected with an Enraf-Nonius MACH3 diffractometer on a crystal with the dimension 0.1 × 0.25 × 0.25 mm. Data collecting range: $4.0° < 2\theta < 54.0°$. Of a total of 4746 collected reflections, 4527 were unique and 2400 with $I > 2\sigma(I)$ observed. The structure was solved by direct methods using SHELX 86. 623 parameters were refined with all data by full-matrix-least squares on F^2 using SHELXL93 (G. M. Sheldrick, Göttingen 1993). All non-hydrogen bonds were refined unisotropically. The hydrogen atoms were fixed in idealized positions using a rinding model. Final R-values: $R1 = 0.0906$ $\{[I > 2\sigma(I)]$ and $wR2$ = 0.2133 (all data) with $R1 = \Sigma|F_o - F_c|/\Sigma F_o$ and $wR2 = \Sigma w\ |(F_o{}^2 - F_o{}^2)^2|/\Sigma w(F_o{}^2)^2\}^{0.5}$; largest peak (0.335 eÅ^{-3}) and hole (−0.288 eÅ^{-3}). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. any request to the CCDC for this material should quote the full literature citation and the reference number 183/142.

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