The molecular world cup: synthesis of a fullerene-calix[4]arene conjugate containing two malonamide substituents within the upper rim†

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A molecular counterpart of the football world cup was synthesized by twofold cyclopropanation of C_{60} with a calix[4]arene containing two malonamide substituents within the upper rim.

Chemists have always been fascinated by aesthetically pleasing molecular architectures[1] that exhibit, for example, an appealing shape or high symmetry. The synthesis of a molecular counterpart of a typically billion times larger macroscopic object, like a cube, a chain, a wheel, a propeller, has always been a challenging goal in itself.[1] For several years we have been investigating the chemistry of two types of molecules that have macroscopic counterparts,[2,3] namely, the football-shaped fullerenes[4] and the bowl-shaped calixarenes.[5] Inspired by the forthcoming football world championship 1998, we realized that a specific assembly of these two building blocks would give rise to a molecule that looks like the FIFA World Cup (Fig. 1). We decided to face this synthetic goal during the period of the world championship and if successful to dedicate this achievement to the winning team. Two days before the final game, on July 9th, the synthesis of the molecular world cup **1** was accomplished.

As a suitable calixarene precursor we synthesized the bidendate derivative **2**[6] in order to apply for the first time a regioselective tether-directed biscyclopropanation of C_{60} with malonamide substituents (Scheme 1), in analogy to the biscyclopropanation with malonates[7] in the presence of DBU–CBr_4.[8] However, in contrast to tether-controlled functionalization of C_{60} with bismalonates it turned out that (1) the addition of the base DBU promoting the formation of the intermediate bromo malonate and its subsequent deprotonation has to be carried out in small portions *via* a titration and (2) that a stepwise synthesis *via* the monoadduct **3**[9] provides better yields of **1**. This is probably due to side reactions of the amide functionalities. The formation of the monoadduct **3** was monitored by TLC (SiO_2 ; CH_3OH–$CHCl_3$ = 5:95; R_f = 0.5). After the addition of 0.25 equiv. DBU the reaction was stopped by quenching with 1 N hydrochloric acid, since pronounced side reactions leading to the formation of more polar products increasingly gained importance. After separation with column chromatography (SiO_2 ; CH_3OH–$CHCl_3$ = 3:97), **3** was obtained in 8% yield as a brown solid. For the synthesis of **1**, 900 μL of 0.030 molar solution of CBr_4 in CH_2Cl_2 was added to 30 mg (0.018 mmol) of **3** dissolved in 20 mL CH_2Cl_2. This mixture was titrated with 960 μL of a 0.047

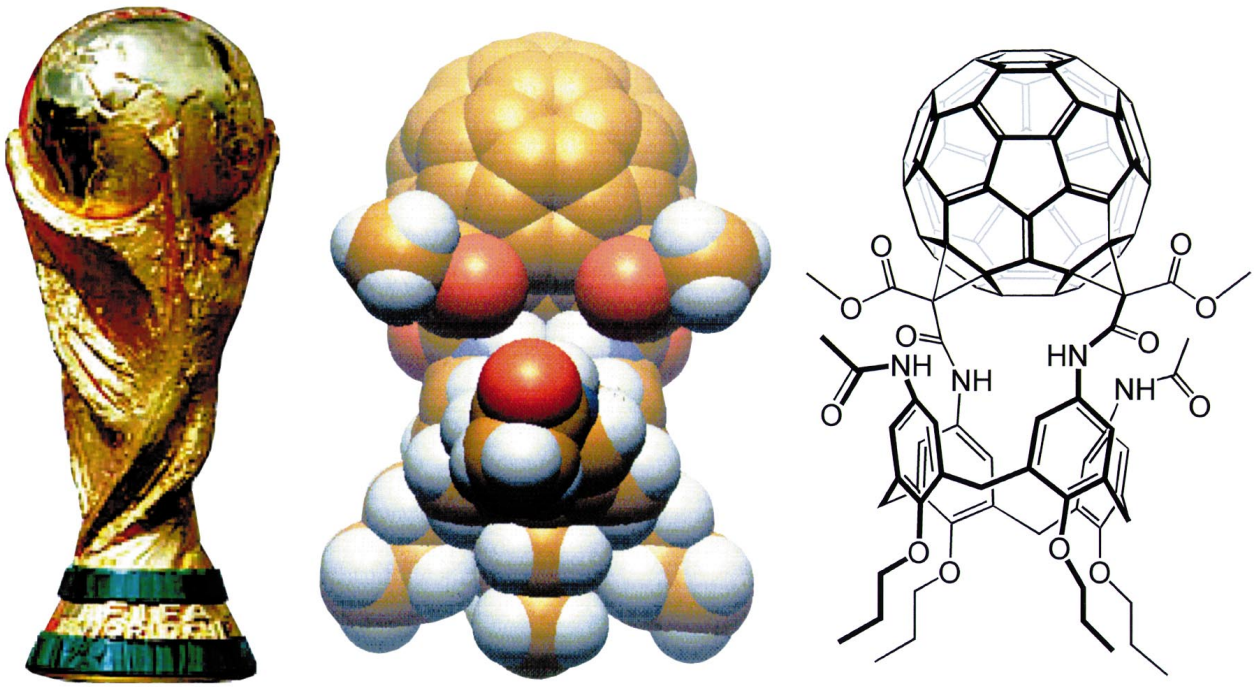
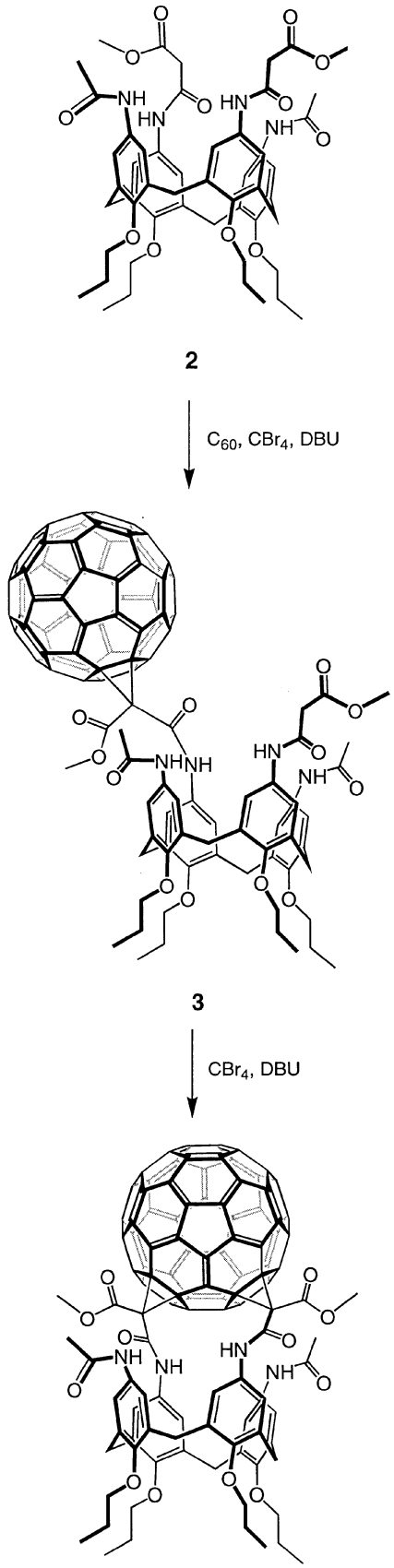


Fig. 1 Shape relationship of the football world cup (left) with the fullerene-calix[4]arene conjugate **1** as a PM3-calculated space-filling model (middle) and a schematic VB structure representation (right).

† A scientific tribute to the French football team 1998.



Scheme 1

molar solution of DBU in CH_2Cl_2 over a period of 90 min. The formation of **1** was monitored by TLC (SiO_2; $CH_3OH : CHCl_3 = 5 : 95$; $R_f = 0.8$). After quenching the reaction mixture with 1 mL of 1 N hydrochloric acid and chromatography on SiO_2 (CH_3OH–$CHCl_3 = 3 : 97$), 13 mg (43%) of **1** was obtained as an orange-brown solid.

Adducts **1** and **3** were completely characterized by ^1H, ^{13}C, ^1H-^1H COSY and ^1H-^{13}C COSY NMR and UV/Vis spectroscopy, as well as by mass spectrometry.[10] The C_s symmetry of the monoadduct **3** with the mirror plane bisecting two phenyl rings carrying the malonyl substituents is clearly reflected by NMR spectroscopy. For example, in the ^1H NMR spectrum of **3** the acetamide methyl protons give rise to one signal whereas two signals for the malonamide methyl protons are observed. For the same reason three singlets for the three magnetically different amido protons with an intensity ratio of 1 : 1 : 2 and four singlets for the four magnetically different aromatic protons are observed. The methylene protons of the calixarene macrocycle produce two overlapping sets of AB systems. The corresponding distribution of signals due to magnetically inequivalent subunits is reflected in the ^{13}C NMR spectrum, where, for example, two signals for the two different methylene C atoms of the calixarene ring at $\delta = 30.88$ and 31.04, one signal for the sp^3 C atoms of the fullerene core at $\delta = 73.04$ and four signals for the aromatic *C*H atoms at $\delta = 119.69$, 120.20, 120.36 and 120.54 are observed. In the region between $\delta = 139$ and 146 appear the 30 magnetically inequivalent fullerene sp^2 C atoms giving rise to 25 clearly resolved signals. The electronic absorption spectrum of **3** is that of a typical monoadduct of C_{60} with the characteristic peak at 426 nm.[4]

The NMR spectra of **1** also unambiguously reveals C_s symmetry of the molecular world cup. In this case the mirror plane bisects the fullerene cluster and the phenyl rings carrying the acetamide substituents, which is reflected, for example, by: (1) one signal at $\delta = 3.68$ for the methoxy protons of the malonyl moiety, (2) two signals at $\delta = 1.69$ and 1.98 for the methyl protons of the acetamide substituents, (3) three signals for the three magnetically inequivalent amide protons at $\delta = 9.37$, 9.60 and 9.98 with an intensity ratio of 1 : 1 : 2, (4) two resonances for the two different methylene C atoms of the calixarene ring at $\delta = 30.61$ and 30.77, (5) two signals for the fullerene sp^3 C atoms at $\delta = 67.92$ and 72.99 and (6) 28 resolved lines for the expected 30 signals (two lines are due to closely overlapping signals) for the fullerene sp^2 C atoms between $\delta = 132$ and 152, with four of them at $\delta = 151.42$, 133.82, 133.61 and 132.77 having half intensity. The latter four resonances are due to the four C atoms located in the mirror plane.

Excluding geometrically unrealistic structures like *cis*-1 or in/in isomers, only the out/out-*cis*-2 or out/out-*trans*-4 isomers are compatible with the NMR spectra. However, comparison of ^{13}C NMR spectra reveals good correlation of **1** with other *cis*-2 rather than with *trans*-4 adducts, since, for example, only *cis*-2 isomers show the characteristic signal with single intensity at $\delta = 151$ also present in **1**.[11] UV/Vis spectra are very characteristic fingerprints for the addition pattern of a bismethanofullerene.[11] The spectrum of **1** clearly reflects a *cis*-2 addition pattern. MM+ force field calculations predict the strain energy of the *cis*-2 isomer to be 7 kcal mol^{-1} lower than that of the *trans*-4 isomer. Geometry optimization of both isomers gives rise to space-filling models that show an impressive shape relationship with the FIFA football world cup (Fig. 1).

Investigations on the electronic, photophysical and complexation properties of **1** and **3** are currently underway.

Notes and references

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10 Selected spectroscopic data of **1** and **3**: **1**: MS (FAB, NBA): 1653 (M^+). UV ($CHCl_3$) λ_{max}/nm: 258, 323, 380. ^{1}H NMR (400 MHz, DMSO-d_6–CD_2Cl_2) δ: 0.72 (m, 6H), 0.98 (t, 6H), 1.69 (s, 3H), 1.70–1.79 (m, 8H), 1.98 (s, 3H), 2.95 (dd, 4H), 3.50 (m, 4H), 3.68 (s, 6H), 3.84 (m, 4H), 4.24 (d, 2H, J = 13.2 Hz), 4.29 (d, 2H, J = 13.2 Hz), 5.67 (d, 2H, J = 2.7 Hz), 6.30 (d, 2H, J = 2.7 Hz), 7.25 (s, 2H), 7.41 (s, 2H), 9.37 (br s, 1H, NH), 9.60 (br s, 1H, NH), 9.98 (br s, 2H, NH). ^{13}C NMR (100 MHz, DMSO-d_6–CD_2Cl_2) δ: 9.40, 9.58, 10.62, 22.47, 22.74, 23.26, 23.59, 24.02, 30.61, 30.77, 67.92, 72.99, 76.07, 76.49, 76.77, 119.15, 119.19, 119.92, 123.73, 130.73, 132.77, 132.97, 133.03, 133.61, 133.82, 135.66, 135.77, 135.99, 136.83, 138.19, 140.95, 141.12, 142.83, 143.11, 143.44, 143.48, 143.64, 143.80, 143.95, 144.22, 144.69, 144.79, 144.87, 144.90, 145.11, 145.48, 145.51, 145.59, 145.77, 147.01, 147.05, 147.15, 151.42, 152.58, 153.21, 153.53, 158.05, 164.39, 167.49, 168.11. **3**: MS (FAB, NBA): 1656 (M^+). UV ($CHCl_3$) λ_{max}/nm: 325.5, 426. ^{1}H NMR (400 MHz, DMSO-d_6–CD_2Cl_2) δ: 0.91 (m, 6H), 1.01 (t, 6H), 1.86 (s, 6H), 1.89 (m, 8H), 3.14 (dd, 4H), 3.42 (s, 2H), 3.67 (s, 3H, $COOCH_3$), 3.74 (m, 4H), 4.06 (s, 3H), 4.41 (d, 2H, J = 12.7 Hz), 4.42 (d, 2H, J = 12.9 Hz), 6.61 (br s, 2H, Ar—H), 6.74 (br s, 2H, Ar—H), 7.18 (br s, 2H, Ar—H), 7.33 (br s, 2H, Ar—H), 9.17 (br s, 2H, NH), 9.84 (br s, 1H, NH), 11.17 (br s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6–CD_2Cl_2) δ: 9.59, 9.67, 10.12, 22.55, 22.59, 22.86, 23.39, 30.88, 31.04, 43.25, 51.76, 56.54, 73.04, 76.47, 76.53, 76.76, 78.70, 119.69, 120.20, 120.36, 120.54, 132.58, 132.71, 132.80, 133.63, 135.43, 135.67, 137.15, 139.47, 140.42, 141.62, 141.88, 141.92, 142.55, 142.62, 142.66, 142.71, 143.53, 143.58, 144.04, 144.09, 144.27, 144.39, 144.45, 144.52, 144.77, 144.83, 144.86, 145.25, 145.55, 145.72, 147.52, 152.05, 153.09, 153.38, 153.82, 159.06, 163.32, 163.42, 164.83, 167.84, 168.46.
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