# Efficient Preparation of Monoadducts of [60]Fullerene and Anthracenes by Solution Chemistry and Their Thermolytic Decomposition in the Solid State

**Bernhard Kräutler,* Thomas Müller, and Alvaro Duarte-Ruiz[a]**

*Dedicated to Professor Fred Wudl on the occasion of his 60th birthday*

**Abstract:** The efficient preparation of monoadducts of [60]fullerene and seven anthracenes (anthracene, 1-methylanthracene, 2-methylanthracene, 9-methylanthracene, 9,10-dimethylanthracene, 2,3,6,7-tetramethylanthracene, and 2,6-di-*tert*-butylanthracene) by cycloaddition in solution is described. The seven mono-adducts of [60]fullerene and the anthracenes were characterized spectroscopically and were obtained in good yields as crystalline solids. The monoadducts of [60]fullerene and anthracene, 1-methylanthracene, 2-methylanthracene and 9,10-dimethylanthracene crystallized directly from the reaction mixture. The thermolytic decomposition at 180 °C of the crystalline monoadducts of [60]fullerene and anthracene, 1-methylanthracene, 9-methylanthracene and 9,10-dimethylanthracene all gave rise to the specific formation of a roughly 1:1 mixture of [60]fullerene and the corresponding antipodal bisadducts ("*trans*-1"-bisadducts) of [60]fullerene and the anthracenes. In contrast, the crystalline monoadducts of [60]fullerene and the anthracene derivatives 2-methylanthracene, 2,3,6,7-tetramethylanthracene and 2,6-di-*tert*-butylanthracene all decomposed to [60]fullerene and anthracenes (without detectable formation of bisadducts) upon heating in the solid state to temperatures of 180 to 240 °C. The formation of the antipodal bisadducts from thermolytic decomposition of crystalline samples of the monoadducts was rationalized by topochemical control.

**Keywords:** cycloaddition · Diels–Alder reactions · fullerenes · solid-state reactions · topochemistry

## Introduction

The discovery of the fullerenes by Kroto, Smalley et al.[1] and the development of a preparative method for the synthesis of fullerenes by Krätschmer, Huffmann et al.[2] have introduced polyunsaturated spherical carbon molecules[3, 4] to synthetic chemistry[4, 5] and to other areas in natural sciences.[6, 7] Special interest has been devoted from the beginning to the exploration of means for regioselective exohedral functionalization of the highly symmetric "Buckminsterfullerene" (**1**, [60]fullerene, $C_{60}$) by addition reactions with inorganic or organic addends.[3–16] $C_{60}$ (**1**) represents a particularly versatile scaffold for the covalent exohedral addition of a variety of organic addends.[4, 5] From sequential addition of up to six organic addends to **1** the synthesis of regular, three dimensionally structured molecules by [3 + 2]-cycloaddition,[3, 5] by cyclopropanation,[4, 5, 9] and/or [4 + 2]-cycloaddition reactions was achieved.[4, 5, 7–11] Regular, multiple exohedral functionalization reactions of **1** have opened a new entry to a variety of three-dimensionally structured organic molecules, thereby enlarging the repertoire of programmed molecular components.[17]

Several laboratories have expanded on Wudl's exploratory work[3a,b] on organic cycloaddition reactions with [60]fullerene (**1**) and have exploited the dienophilic reactivity of this electrophilic,[18] polyunsaturated carbon molecule in [4 + 2]-cycloaddition reactions.[4, 5, 8, 10, 15, 16, 19, 20] Cyclic dienes, anthracenes and other polycyclic aromatics proved to represent useful addends in mono- and multiple cycloaddition processes with $C_{60}$.[10b,c, 19, 20] Without exception [4 + 2]-cycloaddition reactions have been found to occur at one of the 30 equivalent (6,6)-bonds of **1**.[5] In spite of this, the preparative scope of multiple cycloaddition reactions frequently is limited by the lack of regioselectivity.[4, 5, 7–11] On top of this, [4 + 2]-cycloaddition reactions are thermally reversible and the Diels–Alder adducts of **1** in solution have a limited thermal stability.[5] This is a problem in some cases, but has been useful in other situations.[9c, 10b,c, 21] The implied reversible addition of 9,10-dimethyl-anthracene to **1** was exploited by Hirsch and co-workers in a clever way to provide an efficient synthetic entry to symmetric hexa-cyclopropanation products

[a] Prof. Dr. B. Kräutler, T. Müller, Dr. A. Duarte-Ruiz
Institute of Organic Chemistry
University of Innsbruck
Innrain 52a, 6020 Innsbruck (Austria)
Fax: (+43) 512/507-2892
E-mail: bernhard.kraeutler@uibk.ac.at

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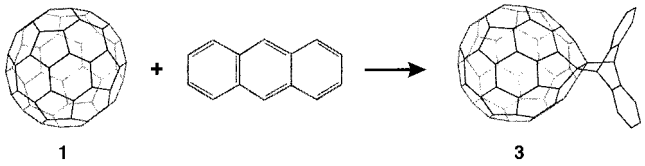
of **1**.[9c] The antipodal ("*trans*-1") bisadduct **2** (of **1** with anthracene),[10b] in which the two anthracene addends are placed at opposing ends (at the poles) of the carbon sphere, opened a concise route to mixed symmetric hexaadducts.[10c] The notorious thermal lability of anthracene adducts of fullerenes[5, 10b, 19] then paved an expeditious way from **2** via the hexaadduct to a known equatorial tetraadduct,[8b] in a transformation (at **1**), which formally represented a first example of an "orthogonal transposition".[10c]

The monoadduct **3** of $C_{60}$ and anthracene (9′,10′-dihydro-[9,10]-ethano-anthraceno-[11′,12′:1,2]-[5,6]fullerene-$C_{60}$, see Scheme 1) was reported as an easily accessible organic derivative of **1**, obtained in 13%[19a] or 25% yield[19b] originally. Various experimental conditions have been explored to improve the yield of the monoadduct **3**: i) microwave irradiation of anthracene and **1** in toluene solution gave



Scheme 1.

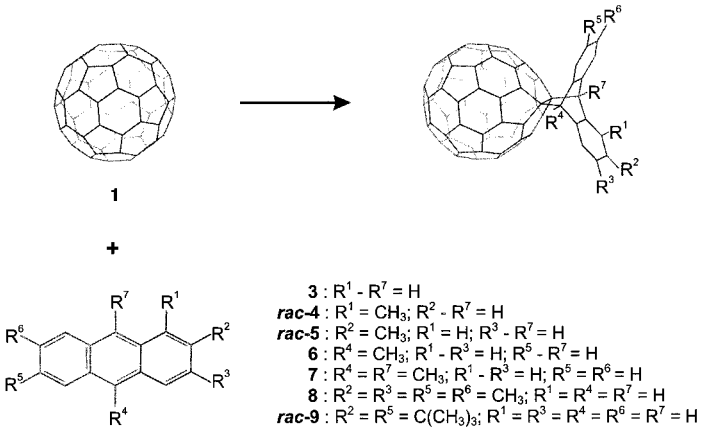
**3** in 35% yield;[22a] ii) reaction of anthracene with **1** at 200 °C in liquid naphthalene gave the monoadduct **3** in 39% yield[22b] and iii) the preparation of **3** in a yield of 55% by means of a high-speed vibration milling technique was reported by Komatsu and his group very recently.[22c] The same strategy turned out to be helpful also to obtain (besides **3**) a mixture of bisadducts of **1** and anthracene (19%) and to prepare monoadducts of **1** with pentacene and with other polycyclic aromatic hydrocarbons.[22c]

We have given some interest to the investigation of [4+2]-cycloaddition reactions as a means of functionalization of $C_{60}$ (**1**)[10, 16b, 23] and developed an efficient synthetic path to the antipodal bisadduct **2** by a topochemically controlled thermal transformation of the crystalline monoadduct **3** (see Scheme 2).[10b] For the purpose of these investigations we have now i) optimized the conditions for the synthesis of the monoadduct **3** in solution and have used similar conditions for the preparation of related adducts of **1** with six simple anthracene derivatives and ii) studied the scope of the thermal solid state transformation of **3** and the other six monoadducts of **1** in the solid state.

## Results and Discussion

**Preparation of monoadducts of [60]fullerene (1) and anthracenes**: The synthesis of monoadducts of anthracenes and [60]fullerene (**1**) has already attracted interest in the earliest studies on organic functionalization of **1**.[3a,b, 4, 5, 19] The expected low thermal stability and the problem of selective mono-functionalization were considered to be severe tasks. A variety of methods were worked out for the preparation of the monoadduct **3**.[19, 22] So far, a solid-state reaction using a "vibrating mill" (vm)-technique gave the best yield of **3** (55%).[22c] Solid-state reactions were also explored in order to prepare the two related monoadducts **6**[24] and **7**,[22c] either with the vm-technique (**7**, 62%)[22c] or by photochemistry (**6**, 30%).[24]

We report here on the efficient preparation of seven monoadducts of anthracenes and [60]fullerene (**1**, $C_{60}$) by addition reactions of the dienophilic electrophile **1** and seven anthracenes in solution and at ambient or lower temperature. Particularly high yields were obtained in several cases by direct crystallization (precipitation) of the monoadducts from the reaction mixtures, thereby inhibiting further addition reactions and thermolytic decomposition (see Table 1 and Scheme 3).

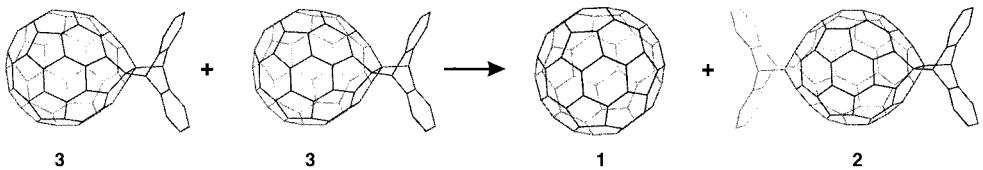



Scheme 3.

Table 1. Preparation of fullerene-anthracene-monoadducts by reaction of anthracenes and **1** in solution (yields of monoadducts **3**–**9**).

| Product | Yield [%][a] | Yield [%][b] |
|---|---|---|
| **3** | 80.0 | 92 |
| *rac*-**4** | 55.2 | 60 |
| *rac*-**5** | 69.9 | 89 |
| **6** | 65.7 | 73 |
| **7** | 73.5 | 90 |
| **8** | 56.0 | 81 |
| *rac*-**9** | 43.0 | 70 |

[a] Yield based on amount of **1** used originally. [b] Yield based on the recovered amount of **1**.



Scheme 2.



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The "anthracene-monoadduct" **3** was prepared by reaction of **1** and anthracene in solution. Monoadduct **3** was obtained in 80.0% yield (92% based on recovered amount of **1**) from a concentrated solution of **1** and anthracene and by exploiting the limited solubility of **3** in 1,2-dichlorobenzene. The monoadduct **3** crystallized from the reaction mixture at room temperature with small contamination by the starting materials and bisadducts. Exposure of the reaction mixture to vapors of methanol (or acetone) increased the amount of the precipitate. A recrystallization of the crude, precipitated **3** from $CS_2$/1,2-dichlorobenzene furnished crystals of nearly uniform **3**, which were suitable for the thermolysis reaction (see below). For analytical purposes the monoadduct **3** was purified by column chromatography before crystallization. The identity of **3** was established on the basis of its UV/Vis-, FAB-MS-, $^1$H NMR and $^{13}$C NMR spectra and by the comparison of these spectra with published data.[19, 22] The UV/Vis-spectrum of a solution of **3** in chloroform had a weak band with a maximum at 706 nm, a sharp band with a maximum at 433 nm and intense bands near 320 nm. The assignment of the signals of aromatic hydrogens in the $^1$H NMR spectrum of **3**, which was not entirely consistent in earlier work,[19a, 22a] could be confirmed by recording a $^1$H NOE-spectrum of **3**. Accordingly, the signal at the lowest field in the spectrum of **3** has to be assigned to the hydrogens at the 1′,4′,5′ and 8′-positions.

The racemic monoadducts *rac*-**4** and *rac*-**5** were prepared by reaction of **1** and 1-methylanthracene or 2-methylanthracene, respectively, using the procedure developed for the synthesis of **3**. Pure racemic monoadducts *rac*-**4** and *rac*-**5** crystallized as black needles from $CS_2$/1,2-dichlorobenzene/pentane. The adduct *rac*-**4** was obtained in 55.2% yield, the isomer *rac*-**5** in 69.9% yield (or 60% and 89%, based on recovered **1**). Both of these monoadducts were structurally characterized by their UV/Vis-, FAB-MS-, and $^1$H NMR spectra. The $^1$H NMR spectra of *rac*-**4** and *rac*-**5** showed each a singlet of the methyl group (*rac*-**4**: at $\delta = 2.68$; *rac*-**5**: $\delta = 2.54$) and two singlets of the bridgehead hydrogen atoms (*rac*-**4**: $\delta = 5.74$ and 6.01; *rac*-**5**: $\delta = 5.71$ and 5.73), consistent with the reduced symmetry of these chiral monoadducts.

The monoadduct of **1** and 9-methylanthracene, 9′-methyl-9′,10′-dihydro-[9,10]-ethanoanthraceno-[11′,12′:1,2]-[5,6]fullerene-$C_{60}$ (**6**), was obtained in 65.7% yield (72.9% based on recovered **1**) from the reaction of **1** and 9-methylanthracene in $CS_2$ at $-20\,^\circ$C. To increase the yield of **6**, which did not precipitate from the reaction mixture, the reaction was interrupted after 24 h and purified in order to separate the product by chromatography from the starting materials. The latter were again dissolved in $CS_2$ and left to react at $-20\,^\circ$C. This procedure was repeated three times. The fractions of chromatographically pure **6** were collected and gave a dark residue. The monoadduct **6**, which was pure according to TLC, was structurally characterized by its UV/Vis-, FAB-MS-, and $^1$H NMR spectra. The $^1$H NMR spectrum of **6** exhibited one singlet at $\delta = 2.80$ (methyl group), one singlet at $\delta = 5.78$ (bridgehead hydrogen) and two multiplets at low field, consistent with $C_s$ symmetry of the monoadduct **6**. The FAB-MS showed a molecular ion at $m/z$ 911.9.

The monoadduct **7** (of **1** and 9,10-dimethylanthracene) was prepared in 73.5% yield (89.7% based on recovered **1**) using the procedure developed for the synthesis of **3**, but with shorter reaction times (twice 24 h) and at lower temperature ($-20\,^\circ$C). The thermally very labile monoadduct **7** crystallized from the reaction mixture at $-20\,^\circ$C and was recrystallized as dark-brown cubes from $CS_2$. It was structurally characterized by its UV/Vis-, FAB-MS-, IR-, and $^1$H NMR spectra. The $^1$H NMR spectrum of **7** exhibited three signals only, consistent with the $C_{2v}$ symmetry of the monoadduct **7**. In the FAB-MS the molecular ion of **7** was recorded as a signal at $m/z$ 925.9.

The monoadducts **8** and *rac*-**9**, of **1** and 2,3,6,7-tetramethylanthracene or of 2,6-di-*tert*-butyl-anthracene, respectively, were both prepared using standard solution chemistry (at room temperature) and chromatographic separation of the reaction mixture. Solutions of the two monoadducts (**8** and **9**) showed only slow decomposition to **1** at room temperature and dark crystals of both monoadducts were obtained from $CS_2$/1,2-dichlorobenzene/pentane. The microcrystalline monoadduct **8** was obtained in 56% yield (81% based on recovered **1**). The monoadduct **9** crystallized as black needles and was obtained in 43% yield (70% based on recovered **1**). The $^1$H NMR spectrum of the monoadduct **8** gave three singlets only (at $\delta = 2.38$, 5.58 and 7.44, rel. int. 6:1:2), consistent with $C_{2v}$ symmetry of **8**. The $^1$H NMR spectrum of *rac*-**9** exhibited five clearly assigned signals, consistent with the $C_2$ symmetry of this chiral monoadduct. The signals at $m/z$ 1010–1013 for the molecular ion of *rac*-**9** in the FAB-mass spectrum were consistent with its deduced molecular formula.

The monoadducts of **1** and the anthracenes investigated here all showed UV/Vis-absorbance spectra very similar to those of **3** and had the characteristics of [4 + 2]-cycloadducts of **1**.[15, 16] The FAB-mass spectra of the monoadducts all showed only a weak signal due to the molecular ion, indicating the efficient fragmentation of [4 + 2]-cycloadducts of **1**, as also noted elsewhere.[19, 22] The positions of the characteristic and well separated signals in the $^1$H NMR spectra of the aromatic hydrogen atoms ($\delta = 7.4$–7.8), the bridgehead ($\delta = 5.5$–6) and methyl group hydrogen atoms ($\delta = 1.42$ for *rac*-**9**, 2.3–2.9 otherwise) were shifted by 0.2–0.4 ppm to lower field (by the fullerene), when compared to the spectra of other 9,10-dihydro-9,10-ethanoanthracenes. The signal pattern reflected the molecular symmetry and the monoadducts **3**,**6**–**8** could be classified as being achiral ($D_{2h}$: **3**,**8**; $C_{2v}$: **6**,**7**), the adducts *rac*-**4**, *rac*-**5**, *rac*-**9** as chiral and racemic ($C_i$: *rac*-**4**, *rac*-**5**; $C_2$: *rac*-**9**), as required due to the low symmetry of the addend (and not due to the addition pattern to **1**). For the $C_2$-symmetric monoadduct *rac*-**9**, the racemic nature was established[26] using a porphinoid $Co^{II}$ complex as chiral shift reagent. The number of signals of the $^{13}$C NMR spectra of **3**, *rac*-**5** and *rac*-**9** were used to determine or estimate the number of nonequivalent carbons and thus to confirm the deduced molecular symmetry of these monoadducts. The bridgehead carbons (9′ and 10′) typically give rise to signals near $\delta = 58$, the saturated fullerene carbons that are directly attached to the anthracene addend, to signals near $\delta = 72$.

The monoadducts **3**, **4**, **5**, **8**, and *rac*-**9** are rather stable at room temperature in solution (storage of solutions of **3** at ambient temperature over a time of 30 days led to about 5%

decomposition to anthracene and **1**). In contrast, the monoadducts bearing methyl groups at the bridgehead positions (i.e., **6** and **7**) decompose rather rapidly under these conditions (at room temperature, about 5% of **6** decomposed within 2 h, for the adduct **7** a half-life of only about 2 h was estimated earlier[22c]). Qualitatively, the same order of reactivity was also found for the formation of these monoadducts by cycloaddition in solution (from an internally standardized NMR analysis): in $CS_2$ solution and for starting concentrations of **1** (2.8 mM) and the anthracenes investigated (5.6 mM), 50% conversion to mono-adducts was analyzed to require a reaction time of about 8 d (12000 min) for anthracene or 2,3,6,7-tetramethylanthracene and 20 d (30000 min) for 2,6-di-tert-butylanthracene, but only 70 min for 9-methylanthracene and less than 5 min for 9,10-dimethylanthracene. The reactivity of substituted anthracenes in their Diels–Alder reaction with maleinic acid anhydride is qualitatively and quantitatively similar.[25] The difference in the stability of the monoadducts studied here, therefore has mainly kinetic rather than thermodynamic origin.

While, with one exception, all of the monoadducts prepared here were obtained in crystalline form, none of the crystals were suitable for a high resolution single crystal X-ray analysis. So far, from the monoclinic crystals of the monoadduct **3** (from $CS_2$/1,2-dichlorobenzene with vapor diffusion of pentane) the characteristics of the unit cell were determined[27] and shown to be basically consistent with the earlier suggested crystal packing (see below).[10b]

**Thermolytic decomposition of monoadducts in the solid state and selective preparation of antipodal bisadducts**: The second major subject of the work reported here concerns the scope of the solid-state transformation of monoadducts of (**1**) and selected anthracenes. The thermolysis of crystalline monoadduct **3** did not lead to a simple fragmentation to **1** and anthracene, as was known from various investigations in solution[19] and as was reported based on thermo-gravimetric experiments with solid monoadduct **3**.[19a] Instead, thermolysis of crystalline **3** at 180 °C for 10 min specifically transformed the monoadduct into about a 1:1-mixture of $C_{60}$ and the antipodal (or "*trans*-1") bisadduct **2**, di{9′,10′-dihydro-[9,10]-ethanoanthraceno-[11′,12′:1,2; 11″,12″:55,60]}-[5,6]fullerene-$C_{60}$), isolated in about 48% yield each (see Scheme 2).[10b] Thermolysis of crystalline **3** was explored initially with smaller amounts (typically about 10 mg) of **3**.[10b] The same results were also obtained with larger quantities of **3** (up to 100 mg, so far); the thermolysis of crystalline **3** revealed itself as an efficient means for the preparation of the antipodal bisadduct **2**. Reduction of the reaction time to 5 min led to about 60–70% conversion (TLC, $^1$H NMR). The bisadduct **2** proved to be rather stable in the crystalline state (decomposition slow at 180 °C). It had a stability in solution only slightly less than **3** and also lost anthracene, to give monoadduct **3**, when heated in solution. The bisadduct **2** thus could be isolated without loss by standard chromatographic and work-up procedures and subjected to a full spectroscopic characterisation. The constitution of the $D_{2h}$-symmetric bisadduct **2** was confirmed spectroscopically.[19b, 22d] The $^{13}$C NMR spectra exhibited only 13 signals, four of them (at $\delta = 58.3$, 125.6, 127.1, and 147.0) of the addends and nine signals of the fullerene carbons (at $\delta =$ 70.2 that of the saturated C atoms directly bound to the anthracene addend). The FAB-mass spectrum of **2** showed a signal of molecular ion at $m/z$ 1076.3. The UV/Vis spectrum of **2** exhibited characteristic intense bands at about 500 nm and 320 nm, a weak maximum near 465 nm and weak and broad absorbance in the visible region, at about 750 nm (see Figure 1 and Experimental Section). The crystal structure of single crystals of **2** has been determined.[27]

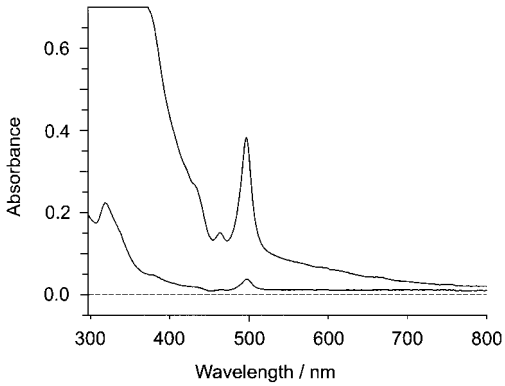


Figure 1. UV/Vis-absorbance spectrum of the antipodal bisadduct **2** (0.076 mM, in $CHCl_3$, 1 cm and 1 mm path lengths, see Experimental Section for details)

Reaction of anthracene with **3** in solution also furnished some of the antipodal bisadduct **2**, but only with small yields and in a mixture with other (far more abundant) regioisomeric bisadducts.[10b, 28] The bisadduct **2** is a frequent side product in the preparation of **3**; the isolation of **2** in small yields has been reported elsewhere.[19b, 22d] The clean solid-state transformation of **3** is therefore a valuable method for the preparation of the bisadduct **2**, which now represents a synthetic platform for further, directed multi-functionalization of **1**.[10c]

The search for the solid-state transformation of **3** into **1** and **2** was initially based on the assumption that the crystals of **3** would be built-up of regular stacks of oriented molecules.[10b] Indeed, from a (powder) X-ray analysis of the crystals of the monoadduct **3** the molecules were deduced to be aligned in linear stacks, in which they have a single orientation. The center-to-center distances between adjacent molecules of **3** were calculated to amount to 12.75 Å.[27] It is not clear, at this stage, whether the individual stacks in a crystal of **3** are all oriented parallel or occur as a mixture of strands with opposite orientations.

Besides a linear stacking of **3** in the crystalline state, two further solid-state properties of the involved fullerene derivative **3** were expected, so that the refunctionalisation of **3** to **1** and **2** was believed to be feasible (see Figure 3 a):

i) The molecular dimensions of two closely packed and oriented molecules of the starting monoadduct **3** were expected to match closely the corresponding pair of closely packed molecules of **1** and antipodal bisadduct **2**. In such a case, it would be likely, that the severe geometric boundary conditions due to the crystal environment[29] would be a less effective factor in inhibiting the reaction.

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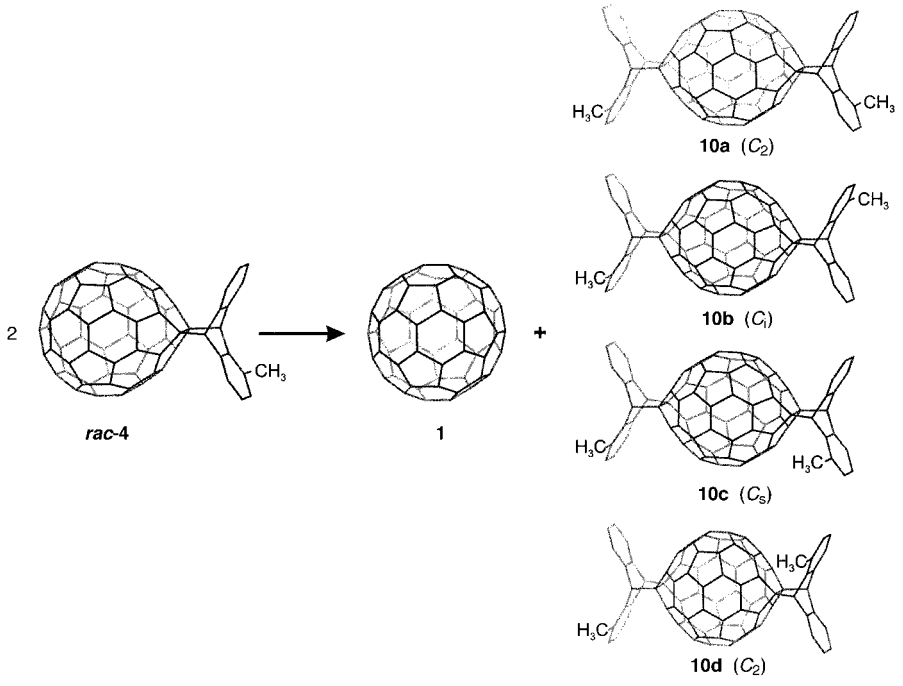
ii) In analogy to crystalline 1′,4′-dihydro-[1,4]-ethano-cyclohexa-1,3-dieno-[7′,8′:1,2]-[5,6]-fullerene-$C_{60}$ (**13**),[10b] two neighboring molecules in a stack of crystalline **3** could be strictly oriented. In a corresponding packing of crystalline **3**, the four saturated C-atoms, which are directly involved in binding of the addend to the fullerene core in molecule **3A** (bridgehead C9′,C10′ and fullerene C1, C2), would be positioned in the same plane as the juxtaposed "backside" C-atoms (C55, C60) of the neighboring molecule (**3B**) in the stack (see Figure 3a). Such an alignment would place C-atoms C55 and C60 of **3B** into the plane defined by the four carbon atoms 1, 2, 9′, and 10′ of its neighbor (**3A**, see Figure a). In this way C55 and C60 would presumably be in the initial trajectory of (C9′, C10′) the anthracene addend leaving the fullerene sphere in the neighboring molecule upon thermal activation.[30] Furthermore, based on the center-to-center distance (12.75 Å) of two nearest neighboring molecules within stacks of crystalline **3**, the distance between the fullerene C-atoms C1/C2 of one molecule of **3** (i.e., of **3A**) and C55/C60 of its neighbor (**3B**) in the stack can be estimated as only about 5.4 Å.[27] With the position of the molecules of monoadduct **3** fixed by the crystal lattice, the crucial four C-atoms therefore would be positioned much closer than required for an aromatic hydrocarbon molecule in direct (but non-bonded) contact with two fullerenes (about 6.3–6.6 Å).[12, 26, 27] On the other hand, they would be close enough pairwise and nearly at distances corresponding to about twice the C–C distances calculated for the transition state in [4+2]-cycloaddition reactions (2.2–2.3 Å).[30] The geometric boundary conditions would thus be given for a concerted cycloreversion-/cycloaddition-process and resulting in a controlled transfer of anthracene between two neighboring molecules of the monoadduct **3**.

The anticipated preparative result, a regiospecific "disproportionation" of **3** into **1** and **2** in the solid-state reaction, was fully born out by the experiments. The specific formation of the bisadduct **2** (along with **1**) accordingly was suggested to be due to a selective transfer of anthracene between two adjacent molecules of **3** in the solid state. The reaction would be subjected to topochemical control.[10b] To test the simple mechanistic model of the transformation of **3** (into **1** and **2**) by transfer of anthracene in the solid state and controlled topochemically by the steric circumstances in the crystal, we have studied the scope of this reaction with six structurally related monoadducts, to be reported below.

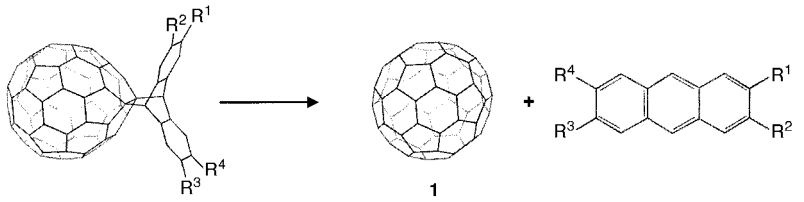
The thermolysis of crystalline monoadduct *rac*-**4** (of 1-methylanthracene and **1**) at 180 °C, 10 min, produced about 43 % each of $C_{60}$ (**1**) and the antipodal bisadduct **10**, which was presumably formed as a mixture of the isomers *rac*-**10a** ($C_2$-symmetric), **10b** ($C_i$-symmetric), **10c** ($C_s$-symmetric) and *rac*-**10d** ($C_2$-symmetric), regioisomeric due to the differing relative position of the methyl group (see Scheme 4). The antipodal (or "*trans*-1")[5] bisadduct **10** was separated from **1** by chromatography. The UV/Vis spectrum of **10** in $CS_2$ exhibited absorbance bands at 502 nm and 468 nm, practically identical to those of **2**. The molecular ion at *m*/*z* 1104 (8 %), fragments at *m*/*z* 912 (7 %) and a base peak at *m*/*z* 720 in the FAB mass spectra of **10** all were consistent with its deduced molecular formula and indicate the high tendency of **10** to undergo fragmentation. A 500 MHz $^1$H NMR spectrum of **10** exhibited three singlets at $\delta = 2.72$, 6.02 and 6.29 (relative intensity 3:1:1), of the methyl group and bridgehead hydrogen atoms, and five complex signals at low field (relative intensity 1:1:2:1:2), due to the aromatic hydrogens. Even at 500 MHz the singlets at high field did split due to the assumed existence of regioisomeric forms of **10**. Low solubility prevented the recording of a significant $^{13}$C NMR spectrum.

Thermolysis of the crystalline (racemic) monoadduct *rac*-**5** (of 2-methylanthracene and **1**) in the solid state resulted in only about 10 % conversion at 180 °C, 10 min, about 80 % conversion at 200 °C, 10 min, and complete conversion after 10 min at 240 °C, according to analysis by TLC and UV/Vis. In all cases, the only products detected were **1** and 2-methylanthracene (Scheme 5).

The monoadduct **6** (of 9-methylanthracene and **1**) was available as a powdery precipitate. The thermolysis of **6** in the solid state and at 180 °C for 10 min, resulted in practically complete conversion (according to TLC) and produced a roughly 1:1 mixture of [60]fullerene (**1**) and the antipodal bisadduct **11**, which was formed as a mixture of the isomers **11a** ($C_{2h}$-symmetric, "*anti*"-isomer) and **11b** ($C_{2v}$-symmetric, "*syn*"-isomer), regioisomeric due to the differing relative position of the methyl groups (see Scheme 6). The UV/Vis

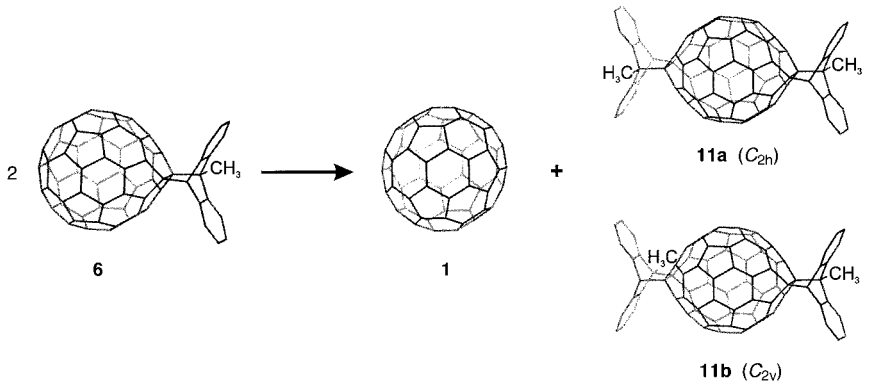



Scheme 4.




***rac*-5** : $R^1 = CH_3$; $R^2 = R^3 = R^4 = H$
**8** : $R^1 = R^2 = R^3 = R^4 = CH_3$
***rac*-9** : $R^1 = R^3 = C(CH_3)_3$; $R^2 = R^4 = H$

Scheme 5.




Scheme 6.

were obtained by extraction of the solid residue from the reaction mixture with $CS_2$ to separate **12** crudely from **1**. The UV/Vis spectrum of **12** in $CS_2$ exhibited absorbance bands at 500 nm and 467 nm, similar to those of **2**. The molecular ion at *m*/*z* 1132 (2%), fragments at *m*/*z* 927 (9%) and a base peak at *m*/*z* 720 all were consistent with the deduced molecular formula of **12** and the high tendency of **12** to undergo fragmentation. A rapidly recorded 200 MHz $^1$H NMR spectrum of **12** exhibited main signals at $\delta =$ 2.95 (singlet of the methyl group H-atoms), at $\delta = 7.47$ and 7.75 (complex signals due to aromatic H-atoms), with relative intensity 3:4:4. Small signals at $\delta = 2.83$ (due to the methyl groups of the monoadduct **7**) and at $\delta = 3.09$ (due to 9,10-dimethyl-anthracene) were already present in the first spectrum obtained, but shifted, when a second $^1$H NMR spectrum was recorded 10 min later

spectrum of crude **11** in $CS_2$ exhibited absorbance bands at 501 nm and 466 nm, similar to those of **2**. The molecular ion at *m*/*z* 1104 (8%), fragments at *m*/*z* 912 (7%) and a base peak at *m*/*z* 720 all were consistent with the deduced molecular formula of **11**. A 300 MHz $^1$H NMR spectrum of crude **11** (see Figure 2) exhibited two signals at high field, each consisting of two barely separated singlets of 1:1 intensity, of the methyl group and bridgehead hydrogen-atoms (relative integrals 3:1), and two complex signals (with relative 4:4 integrals) at low field, due to the aromatic hydrogens. The properties of the signals at high field were consistent with the assumed occurrence of similar amounts of the two regioisomeric forms **11a**/**11b**. In addition to the signals of **11**, signals of much smaller intensity of the monoadduct **6** (relative intensity 0.04) were also present in the NMR spectrum. Low solubility and thermal instability of **11** prevented the registration of a significant $^{13}$C NMR spectrum.

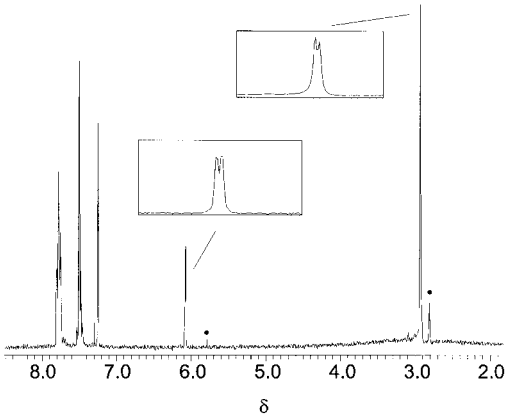
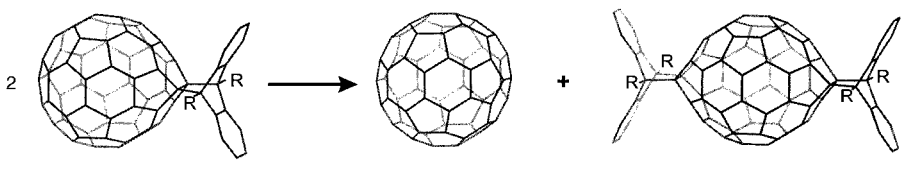



Figure 2. 300 MHz $^1$H NMR spectrum of the reaction mixture obtained from thermolysis of the solid monoadduct **6**, dissolved in $CS_2/CDCl_3 = 3:1$, exhibiting the signals of a 1:1 mixture of the regioisomeric antipodal bisadducts **11a**/**11b**; the signals at $\delta = 2.9$ and 6.1 are doubled, as shown in the expanded inserts (dots mark signals due to the monoadduct **6**).

The thermolysis of crystalline monoadduct **7** (of 9,10-dimethylanthracene and **1**) at 180 °C for 10 min, resulted in complete conversion of **7**. According to the analysis of the crude reaction mixture by TLC a roughly 1:1 mixture of $C_{60}$ (**1**) and the antipodal bisadduct **12** were produced, but the monoadduct **7** and anthracenes were hardly detectable (see Scheme 7). Samples of the crude, thermally unstable antipodal ("*trans*-1")[5] bisadduct **12**




Scheme 7.



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with concomitant decrease of the signals due to the bisadduct **12**.

Thermolysis of the crystalline fullerene-monoadducts *rac*-**4** (of 1-methylanthracene), **6** (of 9-methylanthracene) and *rac*-**9** (of 9,10-dimethylanthracene) all essentially furnished the same outcome as with the monoadduct **3**: in all three cases, thermolysis at 180 °C for 10 min led to complete conversion and resulted in the specific formation of the antipodal bisadducts **10** (43 % from **4**), **11** (ca. 40 % from **6**) and **12** (ca. 40 % from **7**), respectively, besides about 50 % of **1**. The three bisadducts were characterized by their UV/Vis spectra, characteristic of antipodal bisadducts, as well as by their FAB-MS and $^1$H NMR spectra. The bisadduct **10** was (presumably) formed as a mixture of stereo- and regioisomers, due to the low symmetry of the 1-methylanthracene addend. The X-ray analysis of crystalline **10** obtained from a related thermolysis experiment indeed indicated a mixture of all four diastereoisomeric bisadducts with different relative orientations of the methyl group of the addend, but the same (antipodal = *trans*-1) position of the addends.[31] The two regioisomeric forms expected for **11a**/**11b** (methylgroups *syn* or *anti*) of the isomer **11** were indeed indicated in its $^1$H NMR spectrum. In solution, the bisadducts **11** and **12** were rather unstable and had a high tendency to thermally loose their anthracene addends and to revert to the monoadducts **6** and **7** and finally to **1**. The bisadduct **12** thus decomposed during the $^1$H NMR measurements with a half-life of about 10 min at 30 °C.

Similar to the monoadduct *rac*-**5**, thermolysis of the crystalline monoadducts **8** (of 2,3,6,7-tetramethylanthracene and **1**) and racemic monoadduct *rac*-**9** (of 2,6-di-*tert*-butylanthracene and **1**) resulted in gradual decomposition to **1** only and the respective anthracenes at 180 to 240 °C in the solid state (see Scheme 5). In contrast to the results with the four monoadducts **3**, **4**, **6** and **7**, thermolysis of the crystalline monoadducts *rac*-**5** (of 2-methylanthracene), **8** (of 2,3,6,7-tetramethylanthracene) and *rac*-**9** (of 2,6-di-*tert*-butylanthracene) thus did not result in noticeable amounts of the corresponding bisadducts, but rather produced only a mixture of the cycloreversion fragments. The thermolysis of *rac*-**5** and **8** was significantly less effective at 180 °C than that of the monoadduct **3**, so that efficient conversion did not occur at temperatures below 200 °C.

The outcome of the thermolysis of crystalline monoadducts of **1** and anthracenes with a regularly varied pattern of alkyl substituents thus has resulted in a clear "yes/no"-answer: efficient formation of the respective antipodal bisadducts (and **1**) from the monoadducts **3**, *rac*-**4**, **6**, and **7**, but no formation of the corresponding bisadducts from *rac*-**5**, **8**, and *rac*-**9**. Clearly, this result is not the consequence of differing inherent (thermodynamic) stability of the various antipodal bisadducts and monoadducts involved, as i) the variety of antipodal bisadducts formed in the thermolysis experiments spans the whole range of their observed stability and ii) the addition pattern at the fullerene core would not vary within the series of antipodal bisadducts and therefore would not contribute to differentiate between them.

Exploratory control experiments indeed made it likely that **2** would be rather stable in some solid environments, even at 180 °C. This would be the case, in particular, for the hypothetical solid-state environment that would result from the thermolysis of crystalline **3**, that is with stacks of alternating **2** and **1** in 1:1 cocrystals. Heating of 1:1 cocrystals of **1** and **2**, as well as of pure, crystalline **2** to 180 °C for 10 min, that is under the conditions of the thermolysis of **3**, led only to minor decomposition of **2**. Apparently, efficient reaction channels, as available to the crystalline monoadduct **3**, were not accessible to the bisadduct **2** in these crystals. In contrast, a concentrated solution of the monoadduct **3**, when heated to 180 °C, was completely decomposed within 2.5 min. Small amounts of antipodal bisadduct **2** (< 5 %), were indicated to be formed at 180 °C at shorter reaction times, possibly the consequence of residual solid **3** in the reaction mixture. Likewise, the bisadduct **2** would decompose even more rapidly in solution.

The specific formation of antipodal bisadducts **2**, **10**, **11**, and **12**, together with **1**, in the course of thermolysis of crystalline **3**, *rac*-**4**, **6**, and **7** therefore is likely to result from largely hypothetical but relevant boundary conditions in the crystalline solid state, which are

i) kinetically beneficial for the efficient and regioselective antipodal attachment of anthracene or of the involved alkyl-anthracenes, presumably made specific and fast by transfer within ordered stacks of the crystalline monoadducts and
ii) thermodynamically and kinetically beneficial for the stabilization of the aligned 1:1 stacks of antipodal bisadduct molecules alternating with the parent fullerene.

The preparative experiments reported here were primarily intended to explore the synthetic scope of the solid-state transformation of anthracene-monoadducts of the fullerene **1**. At the same time the studies were geared at helping to test aspects of the mechanistic model, involving topochemical control in the solid state. One of the boundary conditions primarily concerned the question of the steric requirements for the hypothetical transfer of anthracenes. The hypothesis of topochemical control and assistance was guided by the assumptions of little over all reorganization in the crystalline lattice during the crucial transfer step, while at the same time the crystalline lattice was supposed to exert tight control in such reactions.[29] The alkyl substituents at the anthracene addends in the monoadducts investigated by the preparative experiments could therefore strongly influence a topochemically controlled reaction.

When considering a likely trajectory for the hypothetical transfer of anthracenes between neighboring molecules in the monoadduct crystals (see Figure 3b), the spatial requirements of an unsubstituted anthracene are covered largely by the space already occupied by the stack, as indicated by the cross section of the fullerene spheres. Methyl groups at the 9- and 10-positions of the anthracene addend would nearly fit within, as well. Methyl groups at the 1-positions of the anthracene addend would also be covered largely by the fullerene cross section along a stack (see Figure 3b, top), while methyl groups at the 2 and 3 (and symmetry-equivalent) positions or other (larger) substituents would clearly stick out from such a "protected" area (see Figure 3b, bottom).

The efficient formation of antipodal bisadducts from thermolysis of the monoadducts **3**, *rac*-**4**, **6**, and **7** could fit well the model of a topochemically controlled transfer of the

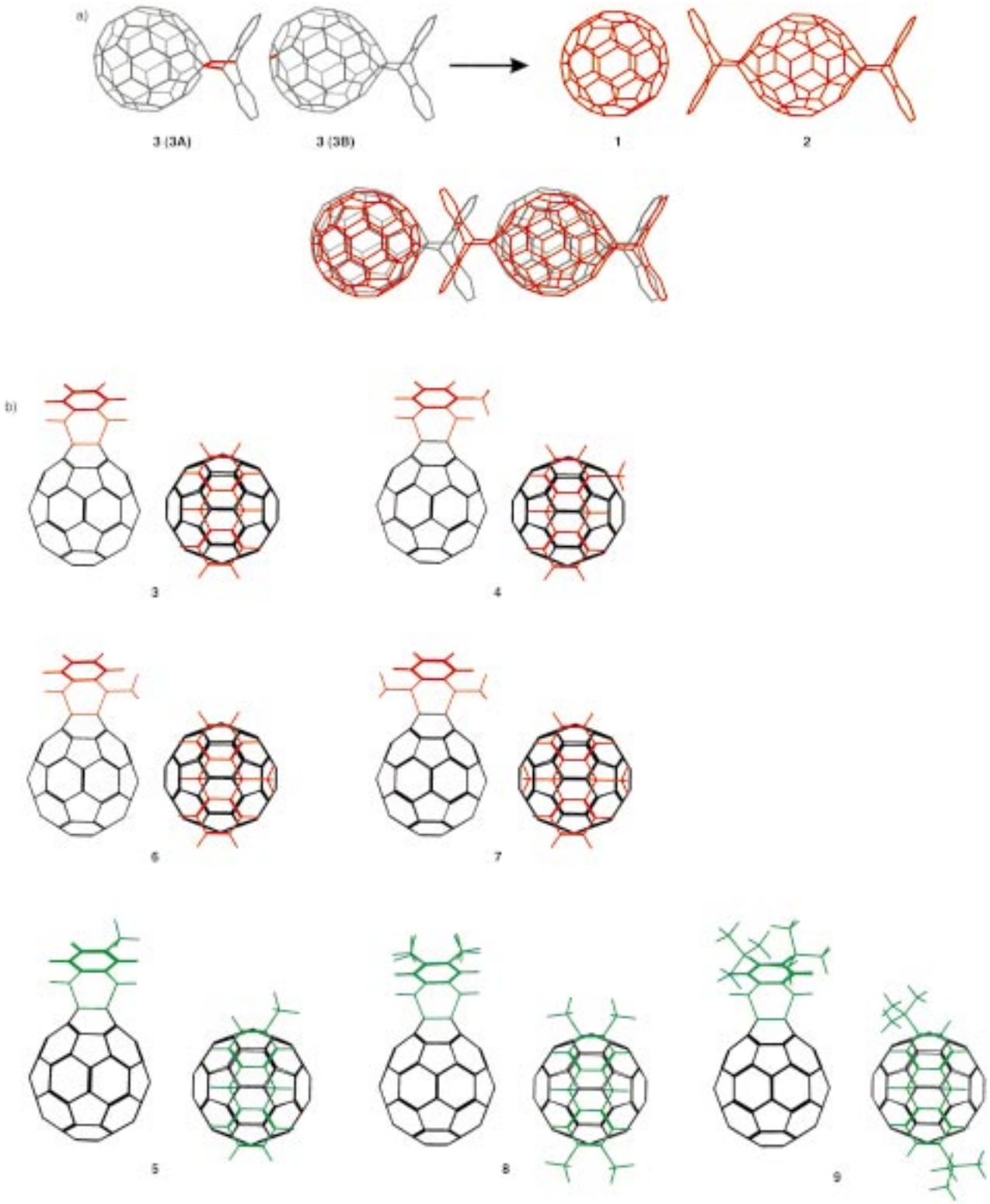


Figure 3. a) Schematic illustration of the topochemical transformation of the monoadduct **3** into the bisadduct **2** and $C_{60}$ (**1**) considering a model, derived from crystal data of **3**.[27] Top: in the crystal two neighboring molecules of **3** (**3A** and **3B**, left), oriented in a stack, are suggested to be transformed into a pair of neighboring molecules, of $C_{60}$ and the antipodal bisadduct **2** (right); **3A** and **3B** are oriented in such a way, as to place carbons C1, C2, C9′, and C10′ of **3A** and C55/C60 of **3B** in a common plane (the corresponding bonds in **3A** and **3B** are colored red). Bottom: A superposition of the pairs of neighboring molecules of **3** (black) and **1** and **2** (red, slightly displaced) illustrates the geometric match of the two pairs. b) Structural stick models of monoadducts **3**–**9** of $C_{60}$ (**1**) and (alkyl substituted) anthracenes (generated with SYBYL, version 6.3A, TRIPOS Assoc., St. Louis, MO) viewed pairwise vertical to the molecular axis and parallel to it. The four adducts displayed at the top (**3**, **4**, **6** and **7**) undergo efficient solid state transformation to the corresponding antipodal bisadducts (**2**, **10**, **11** and **12**), in contrast to the three adducts **5**, **8** and **9**, displayed at the bottom. The projection along the molecular axis allows to compare visually the cross section of the fullerene skeletons and addends (colored red and green) along the (hypothetical) linear stacks in crystals of the monoadducts **3**–**9**.



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respective anthracene moieties. The absence of detectable addition of anthracenes with formation of bisadducts from the monoadducts *rac*-**5**, **8**, and *rac*-**9** could also be traced back to steric control. With the assumption of the relevance of the model of oriented stacks in the crystalline monoadducts *rac*-**5**, **8**, and *rac*-**9**, severe clashes between the anthracenes and the surrounding molecules would be likely.

The alkyl substituent at the anthracene addend would be a significant size- and position-dependent factor in a reaction, which is as tightly controlled sterically as a topochemically controlled reaction involving fullerenes and anthracenes. The experimentally deduced feasibility of specific anthracene transfer reactions in the crystalline monoadducts **3**, *rac*-**4**, **6**, and **7** and the absence of such reactions with the related monoadducts *rac*-**5**, **8**, and *rac*-**9** would therefore fit the structural model of the crystal lattice, in which the monoadduct molecules (of **3**, *rac*-**4**, **6** and **7**) are aligned favorably for the transfer of an anthracene addend under topochemical control between neighboring molecules.

The solid-state reactions of the monoadducts **3**, *rac*-**4**, **6**, and **7** not only produce the corresponding bisadducts with high regioselectivity, but they also typically proceed to high conversion. In the ordered solid state, this reaction thus appears to be favored both kinetically and thermodynamically. Thermodynamic estimates, based on calculated heats of dehydrogenation of 1,9-dihydrofullerene and 1,9,52,60-tetrahydrofullerene (as models for the monoadducts and the antipodal bisadducts, respectively) hint at little enthalpic contributions to the thermodynamic driving force of this reaction.[5, 30b,c] Furthermore, the packing enthalpies within stacks would also presumably not differ much between the two states involved. However, an increase of entropy is a likely contributor to the extent of the investigated transformations. Unsubstituted fullerene molecules often show orientational disorder or reorientational motion in the crystals,[32] which is in contrast crystalline **3**, where the coaxial alignment of the individual molecules is likely to be rather rigid and restricted in its motions.[27]

## Conclusion

The monoadducts of a variety of anthracenes and **1** can be synthesized by solution chemistry at or near ambient temperature with good to high yields. The selectivity and the yields may be increased by precipitation of the adduct from the reaction mixture.

An efficient and specific synthetic path to some antipodal ("*trans*-1") bisadducts of **1** is provided by the thermolysis of suitably structured, crystalline monoadducts of anthracenes. Such antipodal bisadducts of **1** and anthracenes may represent good starting materials for further functionalization of **1**.

The solid-state transformation of the crystalline monoadducts **3**, *rac*-**4**, **6**, and **7** into **1** and the antipodal bisadducts **2**, **10**, **11**, and **12**, respectively, can be rationalized by a model with oriented stacks of the monoadduct molecules and topochemically controlled transfer of the anthracene addends. Studies with the monoadduct **3** and its alkyl-substituted analogues revealed that the steric effects do exert a crucial control over success or failure of the regioselective anthracene transfer reaction in the solid state. Further crystallographic, spectroscopic, and calorimetric work may provide more structural insights in the crystals of mono- and bisadducts of **1** and various anthracenes, as well as quantitative information on the dynamics and the energies involved in their packing and orienting.

## Experimental Section

**General**: *Chemicals*: [5,6]Fullerene-$C_{60}$, Hoechst, lab grade, 96% $C_{60}$, purified[33] or 99.5% from Southern Chem. Group, Texas; 1-methylanthracene, 97%, Aldrich; 2-methyl-anthracene, 9-methyl-anthracene, 9,10-dimethyl-anthracene, methanol, carbon disulfide ($CS_2$, for chromatography), hexane, pentane, all Fluka purum; anthracene, Fluka puriss. scint. grade; 1,2-dichlorbenzene, $CS_2$ and chloroform (for spectroscopy), Fluka puriss.; deuterochloroform, 99.8% D, Cambridge Isotopes, 2,3,6,7-tetramethyl-anthracene,[34] 2,6-di-*tert*-butyl-anthracene;[35] thin-layer chromatography (TLC): POLYGRAMM SIL G/UV 254 plastic plates ($CS_2$/hexane 3:1); column chromatography: silica gel H (for TLC), 5–40 μm Fluka.

*Spectroscopy*: UV/Vis (Hitachi U-3000, $\lambda$ [nm]/log $\varepsilon$), (b)sh = (broad) shoulder. $^1$H NMR: Varian 500 Unity plus (500 MHz), Bruker AM-300 (300 MHz) or Varian Gemini 200 (200 MHz), $\delta$ with $\delta(CHCl_3) = 7.19$. $^{13}$C NMR: Varian 500 Unity plus (125 MHz) or Bruker AM-300 (75 MHz), $\delta$ with $\delta(CDCl_3) = 77.0$. FAB-MS (Finnigan MAT95, *m*/*z* (%)), positive ion detection, Cs gun.

**Preparative experiments**

***Monoadducts of [60]fullerene and anthracenes***

*9′,10′-Dihydro-[9,10]-ethanoanthraceno-[11′,12′:1,2]-[5,6]fullerene-$C_{60}$* (**3**): $C_{60}$ (**1**; 50.0 mg, 0.069 mmol) anthracene (57.0 mg, 0.32 mmol) were dissolved completely in 1,2-dichlorobenzene (3 mL) by using ultrasound at room temperature. The flask with the concentrated solution of the reactants was covered with aluminum foil and stored at room temperature for 24 h with protection from day light. The dark, clear reaction mixture was transferred into a crystallizing dish (6 cm diameter) and the open reaction vessel was put into an desiccator (lower part charged with about 200 mL methanol). Then the reaction mixture was kept in the dark for another 24 h, before it was seeded by addition of a sub-mg amount of micro-crystalline monoadduct **3** (from an earlier batch). After storage of the reaction mixture for six more days at room temperature and in the dark, a significant amount of product had separated off as dark crystallized precipitate. The dark brown supernatant was separated from the precipitate, which was washed with hexane, and the solvents were removed at 35 °C (bath temperature). The crystalline crude product fraction (about 65 mg dry weight), which contained small amounts of **1**, anthracene and bisadducts (according to TLC), and the residue from the dried supernatant, were purified separately by chromatography on a silica gel column (120 g silica gel, *L*: 50 cm, ∅ 3 cm) using a 3:1 mixture of $CS_2$ and hexane as mobile phase. After eluting **1**, fractions containing the pure monoadduct **3** could be collected, followed by fractions containing pure anthracene. The remaining products (mostly bisadducts of **1** and anthracene were also eluted and collected without further separation. All pure chromatographic fractions of **1**, **3**, and anthracene were combined, the solvents were removed using a rotatory evaporator (35 °C bath temperature) and the residues were dried under high vacuum (18 h, 30 °C). The sample containing the higher adducts were worked-up likewise. Thus, **1** (5.6 mg), **3** (48.7 mg), anthracene (9.2 mg) and higher adducts (2.5 mg) were obtained from the crystalline crude product fraction, and **1** (1.2 mg), **3** (1.2 mg), anthracene (32.7 mg) and higher adducts (4.5 mg) from the separation of the supernatant fraction. Altogether, 6.8 mg **1** (9.4 μmol, 13.6%), 49.9 mg **3** (0.055 mmol, 80.0% yield), and 41.9 mg anthracene (0.235 mmol) were obtained as chromatographically pure solids, as well as 7.0 mg of a mixture of higher adducts. Part of the solid monoadduct **3** (47.6 mg) was dissolved in $CS_2$ (1.5 mL) and 1,2-dichlorobenzene (15 mL) and the flask was covered with a pierced aluminum foil and stored in the dark in an desiccator charged with pentane. Needle shaped dark crystals of **3** formed in the course of seven

days, upon which time the monoadduct **3** had almost completely crystallized. Crystalline **3** was separated off from the supernatant and washed with hexane and dried at high vacuum (room temperature, 18 h), to give dark brown crystals (46.8 mg). TLC: $R_f = 0.78$; m.p. $> 180\,^{\circ}C$ (decomp); UV/Vis: ($CHCl_3$, 0.185 mM): $\lambda_{max}$(log $\varepsilon$) = 706 (2.51), 640sh (2.51), 606sh (2.90), 543sh (2.84), 481sh (3.16), 433 (3.51), 408sh (3.63); UV/Vis (1,1,2,2-tetrachloroethane): $\lambda_{max}$(log $\varepsilon$) = 707 (2.49), 640sh (2.55), 542sh (2.95), 497sh (3.13), 481sh (3,14), 462sh (3.16), 434 (3.49), 414sh (3.55), 404sh (3.66), 325sh (4.51), 313 (4.54); FT-IR (KBr): $\tilde{\nu}$ = 2920s, 2851m, 1510m, 1458m, 1425m, 1182w, 758m, 745m, 735m, 698s, 584m, 575m, 561m, 552m, 527s, 490w; $^1$H NMR (300 MHz, $CS_2$/$CDCl_3$ 3:1): $\delta$ = 7.72/7.45 (AA′BB′-System, 8H, H(C2′,C3′,C6′,C7′), H(C1′,C4′,C5′,C8′)), 5.76 (s, 2H; H(C9′,C10′)), assignments from ROESY-experiment; $^{13}$C NMR (125 MHz, ca. 2 mM in $CS_2$/$CDCl_3$ 3:1, ca. 2.4 mM Cr(acac)$_3$): $\delta$ = 155.23 (C3-C60),C4a′,C4b′,C8a′,C8b′), 147.24, 146.14, 145.88, 145.10 (double int.), 145.05 (double int.), 144.34, 142.69, 142.27, 141.96, 141.72, 141.33, 141.28, 139.66, 136.79, 127.09/125.58 (C1′,C4′,C5′,C8′, C2′,C3′,C6′,C7′), 72.26 (C1,C2), 58.26 (C9′,C10′); FAB-MS (NOBA): *m*/*z* (%): 900.5 (8), 899.3(12), 898.3 (5) $[M]^+$, 722.7 (37), 721.6 (95), 720.6 (100) $[C_{60}]^+$.

*1′-Methyl-9′,10′-dihydro-[9,10]-ethanoanthraceno-[11′,12′:1,2]-[5,6]fullerene-$C_{60}$* (*rac*-**4**): $C_{60}$ (**1**; 50.0 mg, 0.069 mmol) and 1-methylanthracene (61.4 mg, 0.32 mmol) were dissolved completely in 1,2-dichlorobenzene (3 mL) by using ultrasound at room temperature. The flask with the concentrated solution of the reactants was covered with aluminum foil and left to react at room temperature for 24 h. Then it was transferred into a crystallizing dish (6 cm diameter) and the open reaction vessel was put into an desiccator, charged with methanol. The reaction mixture was kept in the dark for another 24 h. By that time a dark precipitate had formed and the supernatant was essentially devoid of any fullerene **1** (according to TLC). The brown supernatant was separated from the precipitate, which was washed with hexane. The two product fractions (from the precipitate and from the supernatant) were worked up as described above for the preparation of **3**. Thus, **1** (3.5 mg), *rac*-**4** (31.6 mg), anthracene (1.2 mg) and higher adducts were obtained from the precipitated fraction of crude *rac*-**4**, and *rac*-**4** (3.4 mg), as well as anthracene and higher adducts (69.8 mg) from the separation of the supernatant fraction. Altogether, 3.5 mg **1** (4.9 μmol, 7%) and 35.0 mg *rac*-**4** (0.038 mmol, 55.2%) were obtained as chromatographically pure solids. For further analysis a sample of the solid monoadduct *rac*-**4** was dissolved in $CS_2$ (about 1 mL) and 1,2-dichlorobenzene (10 mL) and the flask was covered with a pierced aluminum foil and was stored in the dark in an desiccator charged with pentane. Needle shaped crystals of *rac*-**4** formed in the course of seven days. TLC: $R_f = 0.88$; m.p. $> 180\,^{\circ}C$ (decomp); UV/Vis ($CHCl_3$, 0.157 mM): $\lambda_{max}$ (log $\varepsilon$) = 705 (2.58), 640sh (2.58), 543sh (3.00), 481sh (3.20), 433 (3.52), 408sh (3.66); $^1$H NMR (300 MHz, $CS_2$/$CDCl_3$ 3:1): $\delta$ = 7.74 – 7.71 (m, 2H; H(C5′,C8′)), 7.59 (d, $J$ = 7.32 Hz, 1H; H(C4′)), 7.48 – 7.42 (m, 2H, H(C6′, C7′)), 7.33 (t, $J$ = 7.3 Hz, 1H; H(C3′)), 7.28(d, $J$ = 7.3 Hz, 1H; H(C2′)), 6.01 (s, 1H, H(C9′)), 5.74 (s, 1H; H(C10′)), 2.68 (s, 3H, $CH_3$), assignments from ROESY-experiment; HSQC/TOCSY (Varian Unity 500, $CS_2$/$CDCl_3$ 3:1): $\delta$ = 129.0 (C4′), 127.5 (C5′,C8′), 127.2 (C3′), 126.0 (C6′,C7′), 123.8 (C2′); FAB-MS (NPOE): *m*/*z* (%): 913.9 (12), 912.9 (17), 911.9 (9) $[M]^+$, 721.9 (55), 720.7 (100), 719.7 (94) $[C_{60}]^+$.

*2′-Methyl-9′,10′-dihydro-[9,10]-ethanoanthraceno-[11′,12′:1,2]-[5,6]fullerene-$C_{60}$* (*rac*-**5**): Analogous to the experiment above (preparation of *rac*-**4**) a solution of $C_{60}$ (**1**; 50.0 mg, 0.069 mmol) and 2-methylanthracene (61.4 mg, 0.32 mmol) in 1,2-dichlorobenzene (3 mL) was left to react at room temperature for 24 h. Then the reaction mixture was transferred into the crystallizing dish and the open reaction vessel was put into the desiccator charged with methanol. The reaction mixture was kept in the dark for another 48 h. By that time a dark precipitate had formed and the supernatant contained higher adducts, but little fullerene **1** (according to TLC). The brown supernatant was separated from the precipitate and the two product fractions (from the precipitate and from the supernatant) were again worked up as described above for the preparation of **3**. Thus, **1** (7.9 mg), *rac*-**5** (40.2 mg), anthracene, and higher adducts (1.2 mg) were obtained from the precipitated crude product fraction, and **1** (2.8 mg), *rac*-**5** (4.1 mg), as well as anthracene and higher adducts (52.6 mg) from the separation of the supernatant fraction. Altogether, **1** (10.7 mg, 14.9 μmol, 21.4%) and *rac*-**5** (44.3 mg, 0.049 mmol, 69.9%) were obtained as chromatographically pure solids. For further analysis a sample of the solid monoadduct *rac*-**5** was dissolved in $CS_2$ (about 1 mL) and 1,2-dichlorobenzene (10 mL) and the flask was covered with a pierced aluminum foil and was stored in the dark in an desiccator charged with pentane. Needle shaped crystals of *rac*-**5** formed in the course of seven days. TLC: $R_f = 0.86$; m.p. $> 180\,^{\circ}C$ (decomp); UV/Vis ($CHCl_3$, 0.175 mM): $\lambda_{max}$ (log $\varepsilon$) = 705 (2.45), 641sh (2.45), 543sh (2.90), 481sh (3.08), 433 (3.44), 408sh (3.57); $^1$H NMR (300 MHz, $CS_2$/$CDCl_3$ 3:1): $\delta$ = 7.72 (m, 2H; H(C5′,C8′)), 7.61 (d, 1H; H(C4′)), 7.55 (s, 1H; H(C1′)), 7.45 (m, 2H; H(C6′,C7′)), 7.26 (d, 1H; H(C3′)), 5.73/5.71 (2s, 2H; H(C10′,HC9′), 2.54 (s, 3H; $CH_3$); $^{13}$C NMR (75 MHz, $CS_2$/$CDCl_3$ 3:1): $\delta$ = 154.93 (C3-C60,C2′,C4a′,C4b′,C8a′, C8b′), 154.78, 146.83, 145.74, 145.48, 144.69, 144.63, 143.96, 143.91, 142.41, 142.28, 141.86, 141.56, 141.29, 141.04, 140.93, 140.89, 140.75, 140.71, 139.31, 139.25, 138.98, 136.89, 136.38, 136.26, 136.20, 132.93, 128.22 (C1′,C4′,C5′,C8′, C3′,C6′,C7′), 126.71, 126.60, 126.36, 125.15, 125.12, 122.97, 71.72 (C1,C2), 58.14 (C9′,C10′), 58.09, 18.50($CH_3$); FAB-MS (NPOE): *m*/*z* (%): 914.9 (7), 913.9 (14), 912.9 (19), 911.9 (11) $[M]^+$, 721.7 (59), 720.7 (100), 719.7 (84) $[C_{60}]^+$.

*9′-Methyl-9′,10′-dihydro-[9,10]-ethanoanthraceno-[11′,12′:1,2]-[5,6]fullerene-$C_{60}$* (**6**): $C_{60}$ (**1**; 100.0 mg, 0.139 mmol) and 9-methylanthracene (53.4 mg, 0.28 mmol) were dissolved completely in $CS_2$ (16 mL) by using ultrasound at room temperature. The flask with the concentrated solution of the reactants was sealed with a stopper and left to react at $-20\,^{\circ}C$ for 24 h. The reaction mixture was purified by flash chromatography on a silica gel column (210 g silica gel H, $L$: 55 cm, ∅ 4 cm), using a 3:1 mixture $CS_2$/hexane as mobile phase. After eluting **1**, fractions containing the pure monoadduct **6** could be collected, followed by fractions containing 9-methylanthracene and then more polar products (mostly bisadducts of **1** and 9-methylanthracene). The chromatographic fractions containing pure **6** were combined and the solvents were removed using a rotatory evaporator (35 °C bath temperature). The chromatographic fractions containing **1** and 9-methylanthracene were combined and the solvents evaporated. The residue containing the re-isolated reactants was redissolved in $CS_2$ (about 10 mL) and allowed to react at $-20\,^{\circ}C$ for 24 h. The reaction mixture was again purified by flash chromatography to isolate a second batch of monoadduct **6** and to re-isolate remaining starting material, as described above. This procedure was repeated two more times. Four samples of chromatographically pure monoadduct **6** were collected and then dried with high vacuum (18 h, 30 °C). The remaining starting fullerene **1** from the last round of chromatographic purification was also re-isolated and dried. Thus, **1** (9.9 mg, 13.7 μmol, 9.9%) was re-isolated and **6** (83.2 mg, 0.091 mmol, 65.7%) was obtained as a chromatographically pure solid, which was analyzed as follows: TLC: $R_f = 0.84$; m.p. $> 180\,^{\circ}C$ (decomp); UV/Vis ($CHCl_3$, 0.182 mM): $\lambda_{max}$ (log $\varepsilon$) = 705 (2.52), 638sh (2.52), 543sh (2.97), 493sh (3.10), 433 (3.42), 406sh (3.62); $^1$H NMR (300 MHz, $CS_2$/$CDCl_3$ 3:1): $\delta$ = 7.70 (m, 4H; H(C1′,C4′,C5′, C8′)), 7.44 (m, 4H; H(C2′,C3′,C6′,C7′), 5.78 (s, 1H; H(C10′)), 2.80 (s, 3H; $CH_3$); FAB-MS (NOBA): *m*/*z* (%): 914.9 (3), 913.9 (6), 912.9 (8), 911.9 (4) $[M]^+$, 721.9 (65), 720.9 (100), 719.9 (76) $[C_{60}]^+$.

*9′,10′-Dimethyl-9′,10′-dihydro-[9,10]-ethanoanthraceno-[11′,12′:1,2]-[5,6]-fullerene-$C_{60}$* (**7**): $C_{60}$ (**1**; 60.0 mg, 0.083 mmol) was dissolved in $CS_2$ (3.5 mL) and 9,10-dimethylanthracene (20.6 mg, 0.101 mmol) in $CS_2$ (0.5 mL). Both solutions were cooled to 0 °C and then the solution of the fullerene **1** was added to the solution of the anthracene derivative at 0 °C. After 5 min the reaction vessel was stored in a freezer (at $-20\,^{\circ}C$) and left there for 24 h. A dark precipitate formed and the supernatant was removed. The latter was concentrated to about half its volume (using the rotatory evaporator, near 0 °C) and then stored in the freezer for 24 additional hours, whereupon another crop of dark precipitate had formed. The supernatant was removed again, the precipitates were washed with small amounts of pentane and dried (HV, 30 °C). Analysis by TLC indicated the solid crude **7** to contain traces of **1**, but no other nonvolatile components. From the supernatant by chromatography and work-up fullerene **1** (10.9 mg) was reisolated and dried. Thus, **1** (10.9 mg, 15.1 μmol, 18.2%) and **7** (56.7 mg, 61 μmol, 73.5%) were obtained as solids. For spectral analysis, a sample of the monoadduct **7** was recrystallized from $CS_2$ at $-20\,^{\circ}C$. TLC: $R_f = 0.84$; m.p. ca. 180 °C (decomp); UV/Vis ($CHCl_3$, 0.151 mM): $\lambda_{max}$ (log $\varepsilon$) = 704 (2.51), 641sh (2.60), 543sh (3.03), 493sh (3.20), 432 (3.47), 405sh (3.72); $^1$H NMR (300 MHz, $CS_2$/$CDCl_3$ 3:1): $\delta$ = 7.66/7.41 (AA′BB′-System, 8H; H(C2′,C3′,C6′,C7′), H(C1′,C4′,C5′, C8′)), 2.83 (s, 6H; 2$CH_3$); FAB-MS (NPOE): *m*/*z* (%): 928.9 (4), 927.9 (7), 926.9 (8), 925.94 (6) $[M]^+$, 721.9 (67), 720.9 (100), 719.7 (96) $[C_{60}]^+$.

*2′,3′,6′,7′-Tetramethyl-9′,10′-dihydro-[9,10]-ethano-anthraceno-[11′,12′:1,2]-[5,6]fullerene-$C_{60}$* (**8**): $C_{60}$ (**1**; 30.0 mg, 0.042 mmol) and 2,3,6,7-tetrameth-



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ylanthracene (19.5 mg, 0.084 mmol) were dissolved completely by using ultrasound in $CS_2$ (10 mL). The flask with the concentrated solution of the reactants was covered with aluminum foil. The mixture was left to react at room temperature for 31 d and the products were purified by chromatography on a silica gel column (130 g silica gel H, *L*: 30 cm, ∅ 4 cm) using a 3:1 mixture $CS_2$/hexane as mobile phase. After eluting **1**, fractions containing the pure monoadduct **8** could be collected, followed by fractions containing the anthracene derivative and more polar products (mostly bisadducts). All pure chromatographic fractions of **1** or **8** were combined, the solvents were removed using a rotatory evaporator (35 °C bath temperature) and the residues were dried with high vacuum (18 h, 30 °C). Thus, **1** (9.4 mg, 13 μmol, 31.3 %) and **8** (22.2 mg, 0.023 mmol, 56 %) were obtained as chromatographically pure solids. For further analysis a sample of the solid monoadduct **8** was dissolved in $CS_2$ (about 1 mL) and 1,2-dichlorobenzene (10 mL) and the flask was covered with a pierced aluminum foil and was stored in the dark in an desiccator charged with pentane. Needle-shaped crystals of **8** formed in the course of seven days. TLC: $R_f = 0.89$; m.p. > 180 °C (decomp); UV/Vis ($CHCl_3$, 0.136 mM): $\lambda_{max}$ (log $\varepsilon$) = 707 (2.56), 642sh (2.56), 543sh (3.04), 481sh (3.20), 435 (3.58), 408sh (3.73); $^1$H NMR (300 MHz, $CS_2$/$CDCl_3$ 3:1): $\delta = 7.44$ (s, 4H; H(C1′,C4′,C5′,C8′)), 5.58 (s, 2H; H(C9′,C10′)), 2.38 (s, 12H; 4$CH_3$, H(C2′,C3′,C6′,C7′)).

*2′,6′-Di-tert-butyl-9′,10′-dihydro-[9,10]-ethanoanthraceno-[11′,12′:1,2]-[5,6]fullerene-$C_{60}$* (*rac*-**9**): $C_{60}$ (**1**; 30.0 mg, 0.042 mmol) and 2,6-di-*tert*-butylanthracene (4.18 mg, 0.084 mmol) were dissolved completely in $CS_2$ (10 mL) by using ultrasound at room temperature. The reaction mixture was left to react at room temperature for 31 d and then it was worked up, as described above for the preparation of **8**. Thus, **1** (11.9 mg, 16.5 μmol, 39.7 %) and *rac*-**9** (18.0 mg, 18 μmol, 43 %) were obtained as chromatographically pure solids. For further analysis a sample of the solid monoadduct *rac*-**9** was recrystallized, as described above for the preparation of **8**. Needle-shaped crystals of *rac*-**9** formed in the course of several days. TLC: $R_f = 0.90$; m.p. > 180 °C (decomp); UV/Vis ($CHCl_3$, 0.122 mM): $\lambda_{max}$ (log $\varepsilon$) = 708 (2.69), 642sh (2.69), 546 sh (3.15), 459sh (3.38), 434 (3.67), 407sh (3.82); $^1$H NMR (300 MHz, $CS_2$/$CDCl_3$ 3:1): $\delta = 7.71$ (d, $J = 2.2$ Hz, 2H; H(C1′,C5′)), 7.62 (d, $J = 8.1$ Hz, 2H; H(C4′,C8′)) 7.42 (dd, $J = 2.2$, 8.1 Hz 2H; H(C3′,C7′)), 5.68 (s, 2H; H(C9′,C10′), 1.42 (s, 18H; 6$CH_3$); $^{13}$C NMR (75 MHz, $CS_2$/$CDCl_3$ 3:1): $\delta = 155.28$ (C3-C60, C4a′,C4b′,-C8a′,C8b′,C2′,C6′), 155.12, 149.28, 146.82, 145.71, 145.47, 144.75, 144.69, 144.63, 143.96, 143.93, 142.44, 142.25, 141.86, 141.61, 141.34, 141.03, 140.92, 139.24, 139.21, 138.25, 136.43, 124.67 (C1′,C3′,C4′,C5′,C7′,C8′), 123.25, 122.09, 72.07 (C1,C2), 57.90 (C9′,C10′), 34.03 (*C*($CH_3$)), 31.02 (*C*$H_3$); FAB-MS (NPOE): *m*/*z* (%): 1012.2 (10), 1011.2 (13), 1010.2 (6) $[M]^+$, 721.7 (58), 720.7 (100), 719.7 (99) $[C_{60}]^+$.

**Thermolytic decomposition of monoadducts of [60]fullerene and anthracenes in the solid state and preparation of antipodal bisadducts**

***Thermolysis of crystalline 3***: *Di[9′,10′-dihydro-[9,10]-ethanoanthraceno-[11′,12′:1,2;11″,12″:55,60]]-[5,6]fullerene-$C_{60}$* (**2**): A melting point capillary was charged with crystalline monoadduct **3** (9.8 mg, 10.8 μmol), which was then evacuated and sealed. The sealed tube was inserted into the heated bath of a Büchi melting point apparatus and heated at 180 °C for 10 min. The cooled melting point capillary was wiped clean, opened and inserted into a flask, where it was crushed mechanically. The solids were dissolved in $CS_2$ (40 mL) with the help of ultrasound and the solution then was concentrated to about 15 mL. The dissolved reaction mixture was then applied to a chromatographic column with silica gel H (120 g, *L*: 40 cm, ∅ 3 cm) and was separated into the main components, **1** and **2**. The chromatographically pure fractions were collected and united. Thus, **1** (3.7 mg, 5.1 μmol, 47.6 %) and **2** (5.6 mg, 51 μmol, 48 %) were isolated as dark solids. For spectral analysis and the purpose of obtaining single crystals for X-ray analysis, the antipodal bisadduct **2** (6.8 mg) was dissolved in $CS_2$ (10 mL), 1,2-dichlorobenzene (1 mL) was added and the flask was loosely closed with a plug of cotton wool, and stored in the dark for several days. After this time, the supernatant was almost colorless and **2** had separated out as dark crystals. For spectral analysis the crystalline bisadduct **2** was washed with pentane and dried at high vacuum at room temperature. TLC: $R_f = 0.54$; m.p. > 190 °C (decomp); UV/Vis ($CS_2$, 0.151 mM): $\lambda_{max}$ (log $\varepsilon$) = 675sh (2.60), 627sh (2.86), 503 (3.98), 469 (3.46), 440sh (3.78), 426sh (3.88); UV/Vis ($CHCl_3$, 0.076 mM): $\lambda_{max}$ (log $\varepsilon$) = 665sh (2.86), 610sh (3.00), 498 (3.76), 464 (3.40), 432sh (3.63), 377sh (4.02), 320 (4.49); $^1$H NMR (500 MHz, $CS_2$/$CDCl_3$ 3:1): $\delta = 7.79$ (m, 4H) (cf. ref. [19b]), 7.47 (m, 4H), 6.04 (s, 4H); $^{13}$C NMR (125.7 MHz, $CS_2$/$CDCl_3$ 3:1; ≈2,4 mM Cr(acac)$_3$): $\delta = 153.8$ (9s) (cf. ref. [19b]), 147.1, 145.3, 145.2, 144.2, 141.8, 141.7, 140.5, 137.3, 127.2 (d), 125.8 (d), 70.3 (s), 58.5 (d); FT-IR (KBr): $\tilde{\nu} = 2920$s, 2849m, 2361m, 2342m, 1468m, 1458m, 1424w, 1261w, 1215w, 1109w, 1095w, 1078w, 1022w, 758s, 731m, 702s, 667w, 640w, 588m, 532w, 522m; FAB-MS (NOBA): *m*/*z* (%): 1079.3 (9), 1078.3 (10), 1077.3 (12), 1076.3 (9) $[M]^+$, 721.1 (100), 720.1 (96) $[C_{60}]^+$.

***Thermolysis of crystalline* rac-*4***: *Di[1′-methyl-9′,10′-dihydro-[9,10]-ethanoanthraceno-[11′,12′:1,2; 11″,12″:55,60]]-[5,6]fullerene-$C_{60}$* (**10**): A melting point capillary was charged with crystalline monoadduct *rac*-**4** (5.0 mg, 5.5 μmol) and sealed. The sealed tube was inserted into the heated bath of a Büchi melting point apparatus and was heated at 180 °C for 10 min. After work-up as described above (thermolysis of **3**), the dissolved reaction mixture was separated by chromatography on a column with silica gel H (80 g) into the main components, **1** and **10**. The chromatographically pure fractions were collected and united. Thus, **1** (1.7 mg, 2.4 μmol, 43 %) and **2** (2.6 mg, 2.4 μmol, 43 %) were isolated as dark solids. For spectral analysis, a sample of the antipodal bisadduct **10** was dried at high vacuum at room temperature. TLC: $R_f = 0.69$; m.p. >180 °C (decomp); UV/Vis ($CS_2$, 0.103 mM): $\lambda_{max}$ (log $\varepsilon$) = 678sh (2.69), 618sh (2.99), 502 (4.07), 468 (3.57), 438sh (3.89), 427sh (3.98); $^1$H NMR (500 MHz, $CS_2$/$CDCl_3$ 3:1): $\delta = 7.79$ (t, 4H; H(C5′,C8′)), 7.65 (d, 2H; H(C4′)), 7.48 (m, 4H; H(C6′,C7′)), 7.36 (t, 2H; H(C3′)), 7.31 (m, 2H; H(C2′)), 6.29 (s, 2H; H(C9′)), 6.02 (s, 2H; H(C10′)), 2.72 (s, 6H, 2$CH_3$); FAB-MS (NOBA): *m*/*z* (%): 1106.2 (9), 1105.2 (16), 1104.2 (8) $[M]^+$, 913.9 (9), 912.9 (12), 911.9 (7) $[M - (C_{15}H_{12})]^+$, 721.7 (53), 720.7 (100), 719.7 (75) $[C_{60}]^+$.

***Thermolysis of 6 in the solid state***: *Crude di[9′-methyl-9′,10′-dihydro-[9,10]-ethanoanthraceno-[11′,12′:1,2;11″,12″:55,60]]-[5,6]fullerene-$C_{60}$* (**11**): A melting point capillary was charged with solid monoadduct **6** (5.0 mg, (0.0055 mmol) and sealed. The sealed tube was inserted into the heated bath of a Büchi melting point apparatus and heated at 180 °C for 10 min. The cooled melting point capillary was wiped clean, opened and its solid contents were dropped into a flask, where the solids were rapidly dissolved in $CS_2$ (about 2 mL) with the help of ultrasound. The dissolved reaction mixture was rapidly analyzed by TLC: **1** ($R_f = 0.8$, ca. 45 %), **11** ($R_f = 0.68$, ca. 45 %), and traces **6** ($R_f = 0.75$, ca. 10 %). The Vis spectrum of the isolate (in $CS_2$) showed pronounced maxima at 501 nm and at 466 nm (of **6**), as well as a broad, weak maximum near 607 nm (of **1**). A 300 MHz $^1$H NMR spectrum ($CS_2$/$CDCl_3$ 3:1, room temperature), exhibited major signals of a 1:1 mixture of **11a**/**11b**, minor signals of **6** and 9-methylanthracene (with relative integrals of methyl group signals 29:1.2:0.2, respectively): signals assigned to **11a**/**11b** (with relative integrals 3:1:4:4): 7.78/7.48 (AA′BB′-system, H(C2′, C3′,C6′,C7′), H(C1′,C4′,C5′,C8′)), 6.079/6.073 (2s, H($C_A$10′,$C_B$10′)), 2.927/2.921 (2s, 2$CH_3$). For FAB-mass spectral analysis the crude sample of the antipodal bisadduct **11** was first dried at high vacuum at room temperature. FAB-MS (NPOE): *m*/*z* (%): 1106.2 (3), 1105.1 (4), 1104.1 (2) $[M]^+$, 912.9 (4) $[M - C_{15}H_{12}+H]^+$, 721.7 (52), 720.7 (100), 719.7 (99) $[C_{60}]^+$.

***Thermolysis of crystalline 7***: *Crude di[9′,10′-dimethyl-9′,10′-dihydro-[9,10]-ethanoanthraceno-[11′,12′:1,2;11″,12″:55,60]]-[5,6]fullerene-$C_{60}$* (**12**): A melting point capillary was charged with crystalline monoadduct **7** (5.0 mg, 0.0054 mmol) and sealed. The sealed tube was inserted into the heated bath of a Büchi melting point apparatus and was heated at 180 °C for 10 min. After work-up as described above (thermolysis of **6**) the dissolved reaction mixture was rapidly analyzed by TLC: **1** ($R_f = 0.8$, ca. 45 %), **12** ($R_f = 0.65$, ca. 45 %), an anthracene ($R_f = 0.7$) and **7** ($R_f = 0.75$, ca.10 %). A Vis spectrum of the isolate (in $CS_2$) exhibited a sharp maximum at 500 nm and two weaker signals at 467 and 607 nm. A 200 MHz $^1$H NMR spectrum ($CS_2$/$CDCl_3$ 3:1, room temperature) had the signals compatible with a ≈2.5:1:0.4 mixture of **12**, **7** (singlet at $\delta = 2.83$) and 9,10-dimethylanthracene (singlet at $\delta = 3.08$); signals assigned to **12**: 7.75/7.47 (AA′BB′-system, H(C2′,C3′, C6′,C7′), H(C1′,C4′,C5′,C8′)), 2.95 (s, $CH_3$). For FAB-mass spectral analysis the crude sample of the antipodal bisadduct **12** from a related experiment was first dried at high vacuum at room temperature. FAB-MS (NPOE): 1133.2 (4), 1132.2 (2) $[M]^+$, 926.9 (9) $[M - C_{16}H_{14} + H]^+$, 721.7 (54), 720.7 (100), 719.7 (99) $[C_{60}]^+$.

***Thermolysis of crystalline* rac-*5***: A melting point capillary was charged with crystalline monoadduct *rac*-**5** (3.0 mg, 3.3 μmol) and sealed. The sealed tube was inserted into the heated bath of a Büchi melting point apparatus and heated at 200 °C for 10 min. After work-up as described above (thermolysis of **6**) the dissolved reaction mixture was analyzed by

TLC ($CS_2$/hexane 3:1) and by recording its UV/Vis spectrum. The TLC indicated about 80% conversion and presence of **1** ($R_f = 0.8$) and 2-methylanthracene ($R_f = 0.7$), but another spot, as expected for an antipodal or any other bisadduct (of **1** and 2-methylanthracene) was missing. Likewise, the Vis spectrum exhibited the characteristics of **1**, but a maximum near 500 nm, as expected for an antipodal bisadduct **2**, was not discernible.

Corresponding thermolysis experiment with *rac*-**5**, carried out either at 180 °C for 10 min (about 10% conversion) or at 240 °C for 10 min (100% conversion), indicated formation of **1** and 2-methylanthracene, but other products were not formed in significant amounts.

***Thermolysis of crystalline 8***: In experiments carried out as described above (*rac*-**5**), crystalline monoadduct **8** (5.0 mg, 5.2 μmol) was thermolyzed in the solid state at 200 °C for 10 min. Analysis of the reaction mixture (which was dissolved in $CS_2$) by TLC ($CS_2$/hexane 3:1) and by UV/Vis spectroscopy, indicated about 90% conversion and presence of **1** ($R_f = 0.8$) and 2,3,6,7-tetramethylanthracene ($R_f = 0.73$), but spectral or chromatographic properties, as expected for an antipodal or any other bisadduct (of **1** and 2,3,6,7-tetramethylanthracene) were missing. Corresponding thermolysis experiment with **8**, carried out either at 180 °C for 10 min (about 15% conversion) or at 240 °C for 10 min (100% conversion), indicated formation of **1** and 2,3,6,7-tetramethylanthracene, but other products were not formed in significant amounts.

***Thermolysis of crystalline* rac-*9***: In experiments carried out as described above (*rac*-**5**), crystalline monoadduct *rac*-**9** (5.0 mg, 0.0049 mmol) was thermolyzed in the solid state at 180 °C for 10 min. Analysis by TLC ($CS_2$/hexane 3:1) and by Vis spectroscopy of the reaction mixture (dissolved in about 5 mL of $CS_2$), indicated complete conversion and presence of **1** ($R_f = 0.8$) and 2,6-di-*tert*-butylanthracene ($R_f = 0.75$), but spectral or chromatographic evidence, as expected for an antipodal or another bisadduct (of **1** and 2,3,6,7-tetramethylanthracene) was missing.

***Exploratory control experiments***: *Preparation and thermolysis of 1:1 cocrystals of fullerene **1** and antipodal bisadduct **2***: A solution of fullerene **1** (4.2 mg, 0.0058 mmol) in 1,2-dichlorobenzene (1.9 mL, in a small crystallizing dish) was mixed into a solution of antipodal bisadduct **2** (6.3 mg, 0.0058 mmol) in $CS_2$ (7.5 mL). The crystallizing dish containing the homogeneous mixture was covered with aluminum foil and was stored for six days at 0 °C with protection from light in an desiccator charged with pentane (100 mL). After that time, black crystals formed. The nearly colorless supernatant was removed and the homogeneous cocrystallizate was washed with pentane and dried at high vacuum. As described in the section for the preparation of **2**, the cocrystals (2.1 mg) were heated in a sealed and evacuated melting point capillary and were heated at 180 °C for 10 min. The product mixture was completely dissolved in $CS_2$ to be analyzed as follows: i) TLC indicated the presence of **1** and **2** (about 1:1) and traces of monoadduct **3**; ii) a 500 MHz $^1$H NMR spectrum showed the signals of the antipodal bisadduct **2** (singlet at $\delta = 6.00$) and also indicated the presence of a small amount of monoadduct **3** (singlet at $\delta = 5.72$), with relative intensities 15.5:0.6 (±0.5). Anthracene could not be detected. The data are consistent with the presence of about 48% of each of the starting materials (**1** and **2**) and about 4% of monoadduct **3**.

*Thermolysis of crystalline antipodal bisadduct **2***: A sample of crystalline **2** (2.3 mg) was heated to 180 °C for 10 min and analyzed as described above. A 500 MHz $^1$H NMR spectrum of the heated sample showed the signals of the antipodal bisadduct **2** (singlet at $\delta = 6.00$) and indicated the presence of anthracene (signals in the aromatic region) and again a small amount of monoadduct **3** (singlet at $\delta = 5.72$), with relative amounts of **2**, **3** and anthracene of about 90:5:15 (±3). A consistent product analysis was also provided by TLC, which allowed the additional detection of about 10% of free fullerene **1**.

*Thermolysis of monoadduct **3** in solution*: In a sealed glass ampoule an argon saturated solution of monoadduct **3** (1.8 mg) in 1,2-dichlorobenzene (1.8 mL) was heated to 180 °C for 105 s (experiment A) or for 2.5 min (experiment B). The reaction vessel was then cooled with ice externally, opened and the reaction mixture was analyzed by TLC The solvent was then removed under high vacuum and the residue dissolved in $CS_2$/deuterochloroform 2.5:1, to be analyzed by a 500 MHz $^1$H NMR spectrum. While only fullerene **1** and anthracene could be detected as reaction products from experiment B, the NMR spectrum of reaction mixture A indicated anthracene (about 90%), about 10% of **3** (singlet at about $\delta = 5.7$) and about 3% of the antipodal bisadduct **2** (singlet at about $\delta = 6.0$).

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