Regioselective 'One-Pot' Synthesis of Antipodal Bis-adducts by Heating of Solid [5,6]Fullerene-C_{60}-I_h and Anthracenes

Preliminary Communication

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Antipodal ('*trans*-1') *Diels-Alder* bis-adducts **3** and **7**–**9** of [5,6]fullerene-C_{60}-I_h (**1**) with some anthracenes were prepared highly regioselectively by heating mixtures of the solid **1** and anthracene or of (one of) three alkyl-substituted anthracenes in the absence of solvents (*Scheme 2*). Other bis-cycloadducts were not detected, but lesser amounts of mono-cycloadducts **2** and **4**–**6**, respectively, were also formed. Heating of solvent-free mixtures of **1** and three other alkyl-substituted anthracenes did not result in a detectable amount of (antipodal) bis-cycloadducts. The antipodal bis-adduct **7** of **1** and of 1-methylanthracene was analyzed by X-ray crystallography. The preparative outcome of heating of anthracenes and solid **1** parallels the result of the heating of the corresponding crystalline mono-adducts of anthracenes and **1**. Both approaches reveal a remarkably consistent dependence of the reaction upon the presence and position of alkyl substituents at the anthracene unit. The regioselective assembly of antipodal bis-adducts from anthracene(s) and **1** cannot be rationalized by their (inherent molecular) stability, but it indicates the crucial control of the lattice.

Introduction. – Fullerenes, the spherical C-molecules [1–3], are fascinating targets of chemistry, which also have enriched several other areas of the natural sciences [4–6]. The original synthetic interests concerned the preparation of a variety of uniformly (mono)functionalized fullerenes [4][6–8]. More recently, the regio- and stereoselectivity of multifunctionalization reactions of the fullerenes has become a central focus, for the purpose of exploiting the spherical and polyunsaturated nature of the fullerenes [5][6][9–12]. Several elegant synthetic strategies were developed, among these, *Diederich*'s method of 'tether-directed remote functionalization' [5][9] and the 'reversible template-directed activation' of fullerenes, used by *Hirsch, Rubin*, and others [6c][10][12c][13].

The high symmetry and pronounced dienophilic reactivity of the electrophilic [5,6]fullerene C_{60} (**1**) rendered **1** an attractive target for a variety of [4+2]-cycloaddition reactions, which were found to occur at one of the 30 equivalent (6,6)-bonds of **1** exclusively [5][6]. Cyclic dienes, anthracenes, and other polycyclic aromatics proved to represent useful addends in mono- and multiple cycloaddition processes with C_{60} [8][12][14]. The mono-adduct **2** (9′,10′-dihydro[9,10]ethanoanthra[11′,12′:1,9][5,6]fullerene-C_{60}-I_h) of anthracene and of C_{60} can easily be prepared

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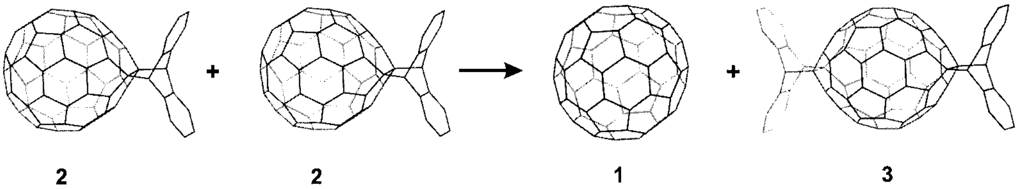
[8e,f] [14] [15]. A highly uniform and efficient synthetic path to the antipodal ('*trans*-1') bis-adduct **3** (9′,9″,10′,10″-tetrahydrobis[9,10]ethanoanthra[11′,12′:1,9;11″,12″:52,60]-[5,6]fullerene-C_{60}-I_h) was found *via* a topochemically controlled thermal transformation of the crystalline mono-adduct **2** (see *Scheme 1*) [15]. Similar solid-state transformations were achieved more recently with the corresponding mono-adducts of **1** and 1-methylanthracene, 9-methylanthracene, and 9,10-dimethylanthracene, respectively (*i.e.* mono-adducts **4**–**6**) [15b]. The selective formation of the antipodal bis-adducts **3** and **7**–**9** from the solid-state reactions was interpreted by a model, in which stacks of the mono-adducts **2** or **4**–**6** would undergo topochemically controlled transfer of anthracene addends to result in the formation of stacks with alternating fullerene and antipodal bis-adduct molecules [15].

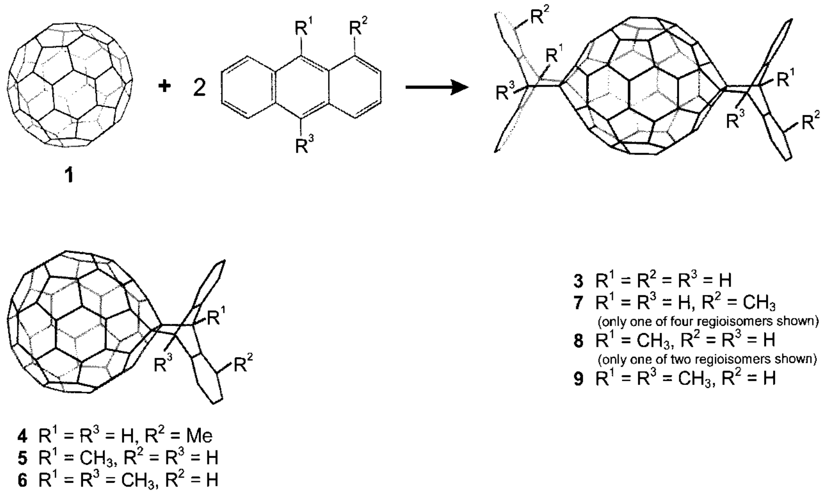
Scheme 1



The *Diels-Alder* reaction of anthracene and the mono-adduct **2** in solution gave five regioisomeric bis-adducts, among which the bis-adduct **3** was a minor product [16a]. Thus, the high regioselectivity observed in the solvent-free high-temperature reactions contrasts the outcome of the bis-addition reactions of **1** and anthracenes in solution [16], as well as that of other bis-cycloaddition reactions with **1** [6b] [6c]. The (modest) regioselectivity of the formation of (up to eight) bis-adducts from cyclopropanation in solution was suggested to be of kinetic rather than of thermodynamic origin [6c] [11]. On the other hand, endohedral ^{3}He-labeled C_{60} was used by *Saunders et al.* [16b] to study the equilibria in solution concerning addition reactions of 9,10-dimethylanthracene: six ^{3}He-signals with relative intensities in the range of 1 to 75 were assigned to (unspecified) bis-addition products, whose inherent stability in solution, therefore, would be similar (within *ca.* 3 kcal/mol) at room temperature. While the thermodynamics and kinetics of cycloaddition reactions at C_{60} in the '*cis*'-mode are controlled sterically by close-by addends, cycloaddition reactions elsewhere on the polyunsaturated fullerene sphere (in '*trans*' and 'e'-positions) experience low selectivity, as rationalized in theoretical studies [6b] [17]. Electrochemically induced migrations of cyclopropyl units in bis-cyclopropanation products of **1** resulted in preferential formation of '*trans*-1' and 'e'-bisadducts of C_{60} [18].

Results and Discussion. – The D_{2h}-symmetric antipodal bis-adduct **3** and the related '*trans*-1' bis-adducts **7**–**9** of C_{60} have recently become available in fair to good yields *via* the solid-state high-temperature reactions of the corresponding crystalline mono-adducts **2** and **4**–**6** [15]. We have now explored the preparative outcome of direct heating of solvent-free mixtures of some anthracenes and of fullerene **1**. As described here, these experiments have resulted in a direct and selective 'one-pot' preparation of the four antipodal bis-adducts **3** and **7**–**9** of C_{60} (see *Scheme 2*).

Scheme 2



3 $R^1 = R^2 = R^3 = H$
7 $R^1 = R^3 = H, R^2 = CH_3$
(only one of four regioisomers shown)
8 $R^1 = CH_3, R^2 = R^3 = H$
(only one of two regioisomers shown)
9 $R^1 = R^3 = CH_3, R^2 = H$

4 $R^1 = R^3 = H, R^2 = Me$
5 $R^1 = CH_3, R^2 = R^3 = H$
6 $R^1 = R^3 = CH_3, R^2 = H$

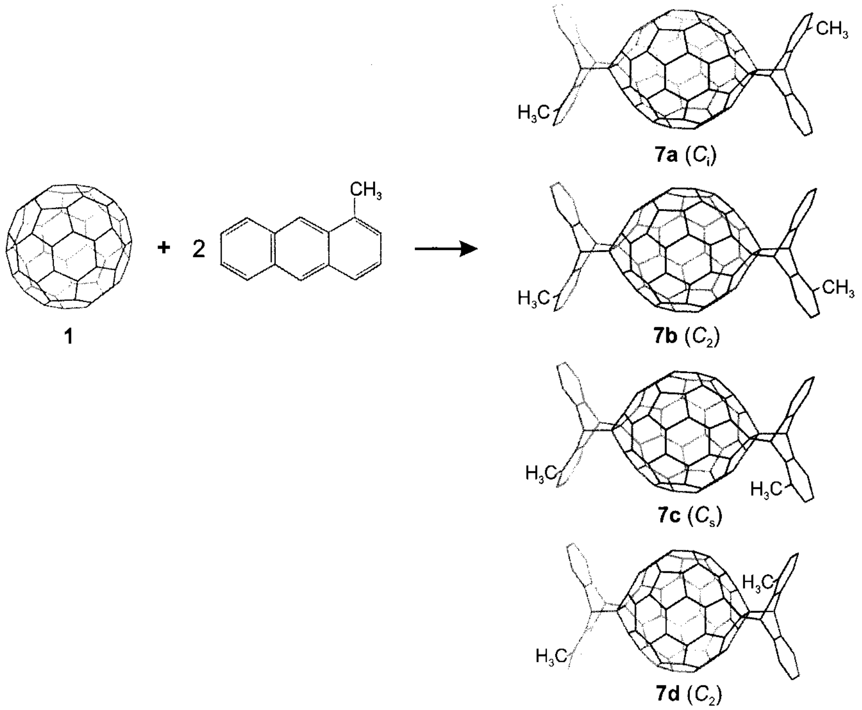
Heating of mixtures of a two-fold excess of anthracene and **1** for 1 h and at 240° in the absence of solvents converted *ca.* 50% of **1** and gave *ca.* 44% of the D_{2h}-symmetric antipodal bis-adduct **3** and traces of mono-adduct **2** (see *Scheme 2*). Other bis-adducts could not be detected. The reaction mixture was separated by column chromatography, and the relevant three components **1**–**3** were isolated as pure compounds and identified spectroscopically [8d–f][14d], and their individual yields were determined.

Likewise, heating of mixtures of **1** and a two-fold excess of 1-methylanthracene at 240° for 30 min converted 36% of **1** and gave *ca.* 23% of the antipodal bis-adduct **7**, besides *ca.* 13% of mono-adduct **4**. The adducts **4** and **7** were identified by their UV/VIS and ^{1}H-NMR spectra [15b], other adducts were not detected by TLC. A 500-MHz ^{1}H-NMR spectrum of **7** showed a single resonance for the Me-group signal and thus did not reveal the expected regioisomeric nature of **7** as a mixture of the antipodal bis-adducts **7a**–**d** (which differ by the relative position of the Me substituent only (see *Scheme 3*)).

Crystals suitable for X-ray-analysis were grown for three samples of the bis-adduct **7** from the high-temperature reaction. The bis-adduct **7** crystallized in the centrosymmetric space group $P2_1/n$, with half a molecule in the asymmetric unit. As discussed below, the crystallographic data showed a rather complex disorder and suggested all four possible regioisomers of **7** to be present in the crystal lattice. The distribution of these isomers could not be quantified well, due to the restrictions by the crystallographic symmetry and two kinds of molecular disorder. Three randomly selected crystals of **7** were investigated, and their crystallographic properties were found not to be significantly distinguishable.

Among the four regioisomers **7a**–**d** of **7**, only **7a** is basically compatible with the observed crystallographic inversion centre (see *Fig. 1*). The overall structure of **7a** is similar to that of **3**, whose crystal structure was also analysed recently [19]. Both antipodal bis-adducts crystallize in the monoclinic space group $P2_1/n$. In the crystals of **7**, the anthracene addends were found to have disordered positions, as shown in *Fig. 2*.

Scheme 3



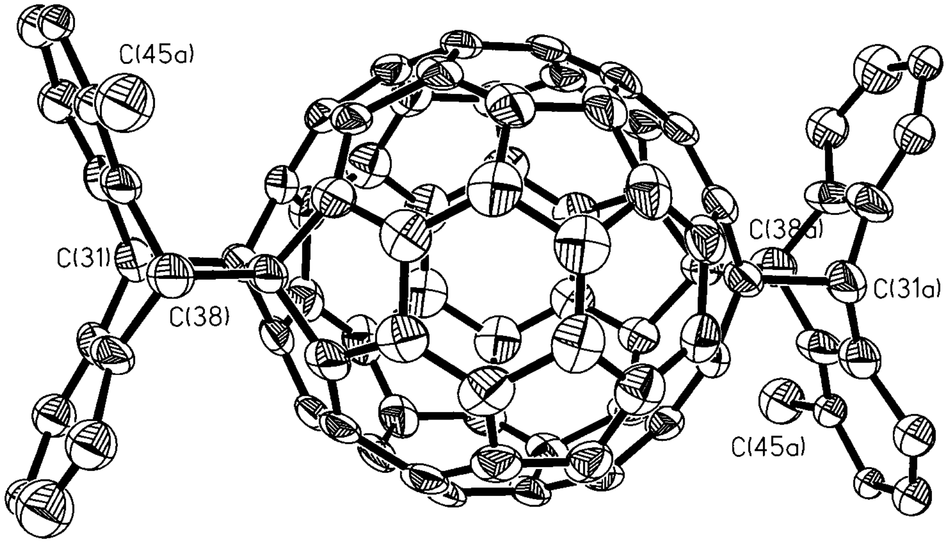


Fig. 1. *Molecular structure of the antipodal bis-adduct isomer* **7a** (ORTEP plot, 40% probability ellipsoids). Arbitrary numbering.

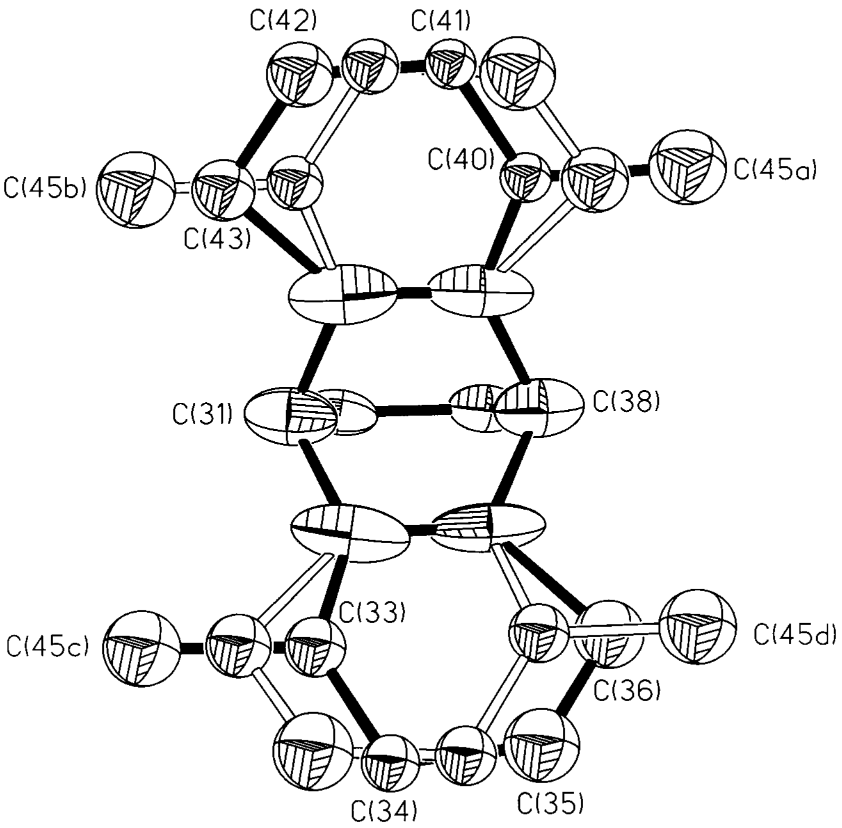


Fig. 2. *Structure of the anthracene addend of the antipodal bis-adduct* **7**, *distorted by orientational and positional disorder* (ORTEP plot, 40% probability ellipsoids). Arbitrary numbering.

This disorder could be separated into *i*) a nearly 1:1 orientational disorder of the molecule, and *ii*) a positional disorder of the Me group with approximate occupancy factors C(45a)/C(45b)/C(45c)/C(45d#) of 0.4:0.2:0.2:0.2. The first type of disorder could be rationalized by steric requirements of the Me group of one molecule close to the anthracene wing of the neighbour. The second one is likely to be due to the presence of the four regioisomers **7a – d** as a mixture (rather than of a disordered single isomer, such as **7a**). The observed non-statistical occupancy was analysed with a model, assuming the distribution of the isomers **7a – d** to be roughly statistical and examining the environment of one molecule in the crystal lattice. The molecules form a sheet perpendicular to the crystallographic [1 0 – 1] axis with shape-complementary concave-convex motifs (see *Fig. 3*). The bonds C(40)–C(45a) and C(33)–C(45c) are oriented roughly in the direction of the sheet, while the bonds C(43a)–C(45b) and C(36a)–C(45d) point out-of-plane in direction to the next one. The distribution of the regioisomers is subjected to two observable restrictions, considering the positions of the Me groups. Within the sheet, the position C(45a) and C(45c#) of two neighbouring anthracene units can not be occupied, as the distance between them would only be

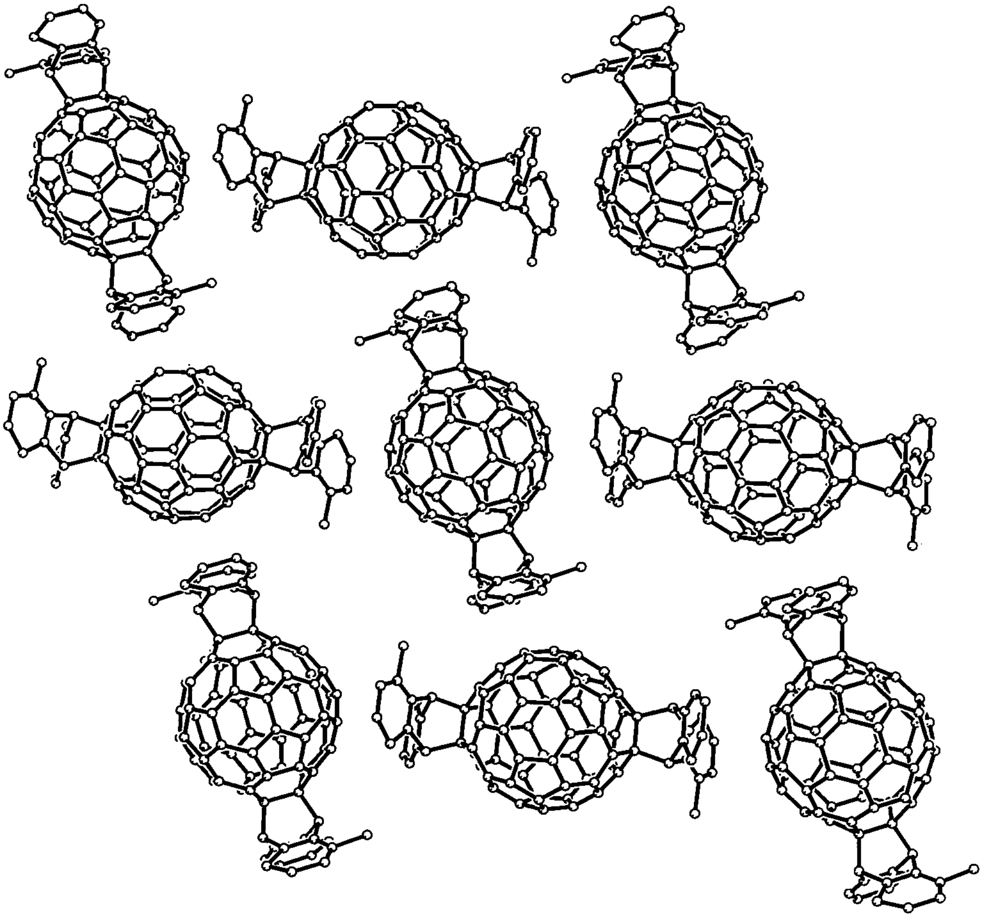
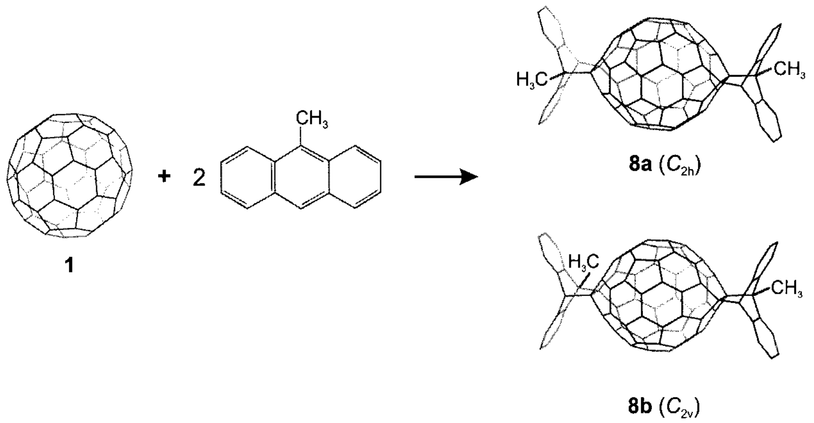


Fig. 3. *Packing of a sheet of antipodal bis-adduct isomer* **7a**, *viewed down the crystallographic [1 0 – 1] axis*

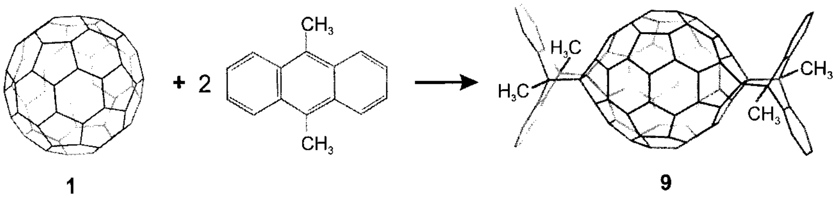
2.881 Å. Likewise, the occupancy of both C(45b) and C(45d) of two anthracene wings of two adjacent sheets would lead to an irregular distance of 2.584 Å. The preferred occupancy of position C(45a), which is twice that of the other positions, can result from: *i*) the Me positions C(45b) and C(45d) are 'out-of-plane' and increase the crystal volume; *ii*) in the crystal, the position C(45a) experiences less steric hindrance than C(45c): the nearest H-atoms of two neighbouring molecules are at a distance of 3.633 Å (H(31#)) from C(45a) and at 2.965 Å (H(38#)) only from C(45c). The non-statistical occupancy thus can be rationalized based on packing effects, and the data of all three samples are interpreted best as being due to a (presumably statistical) mixture of four regioisomers **7a – d**, rather than of a disordered single isomer.

Heating of mixtures of C_{60} and of a twofold excess of 9-methylanthracene at 200° for 30 min converted *ca.* 50% of **1** (mostly to **8**, according to TLC) and gave *ca.* 33% of the thermally labile antipodal bis-adduct **8**, besides 16% of mono-adduct **5**. The adducts

Scheme 4



Scheme 5



5 and **8** were identified UV/VIS- and ^{1}H-NMR-spectroscopically [15b]. The ^{1}H-NMR spectrum indicated **8** to consist of a 1:1 mixture of two isomers, as found from thermolysis of the solid mono-adduct **5** [15b] and consistent with the expected availability of the C_{2h}-symmetric **8a** and the C_{2v}-symmetric **8b** (see *Scheme 4*). Likewise, heating of 1:2 mixtures of **1** and 9,10-dimethylanthracene at 240° for 60 min converted *ca.* 50% of **1** into the bis-adduct **9** (*Scheme 5*) and some mono-adduct **6** (according to TLC). After a rough separation of the products, *ca.* 20% of the thermally very labile antipodal bis-adduct **9** [15b] were obtained, besides *ca.* 22% of mono-adduct **6**, but again no other bis-adducts were detected (see *Scheme 2*).

In contrast, heating of 1:2 mixtures of solid fullerene **1** and 2-methylanthracene, 2,3,6,7-tetramethylanthracene, or of 2,6-di(*tert*-butyl)anthracene, respectively, at 240° for 60 min (30 min in the case of 2-methylanthracene) did not result in any noticeable conversion of **1**, and neither antipodal bis-adducts nor even (significant amounts of) mono-adducts were detected.

The practically exclusive formation of antipodal bis-adducts from **1** and certain anthracenes on heating 1:2 mixtures of the solid components is unmatched by corresponding addition reactions in solution [16]. The experimental procedure is simple and leads to the thermally unstable antipodal (or '*trans*-1') bis-adducts **3** and **7**–**9** selectively and in fair to good yields. Antipodal bis-adducts are of interest, as they represent useful platforms for further selective and regular multi-functionalization of **1** [12c]. However, the reaction reported here has limited scope, and the formation of bis-adducts was not found in the high-temperature reaction of **1** with some substituted anthracenes, in a striking parallel to the result of the solid-state transformations of the corresponding bis-adducts [15]. These observations point to the (thermodynamic) relevance of packing effects in the assembly of the antipodal bis-adducts, as delineated further below.

The efficient (and remarkably exclusive) assembly of antipodal bis-adducts from **1** and some anthracenes in their solvent-free mixtures was achieved at temperatures above the melting point of the anthracenes used (with the exception of 2,3,6,7-tetramethylanthracene) [20] and where the crystalline bis-adduct **3**, as well as 1:1 cocrystals of **1** and **3**, would already decompose slowly [15b]. At these temperatures, mono- and bis-adducts (such as **2** and **3**) would be expected to decompose rapidly in solution: In (dilute) solution, the bis-adducts **8** and **9** are unstable thermodynamically [16b] (at 30°, **9** has a half life of *ca.* 10 min [15b]).

In the present work, the high-temperature experiments were carried out under conditions which presumably approach even those of thermodynamic control. However, the observed exquisite selectivity for the assembly of antipodal bis-adducts can not be rationalized based on their inherent stability, as compared to that of the other possible bis-adduct regioisomers [16]. Roughly 1:1 mixtures of C_{60} and of antipodal anthracene bis-adducts (such as **3**) appear to be characteristic and presumably the essential components of the high temperature reaction mixtures. Applying the model developed earlier [15], these products could assemble into stacks with alternating C_{60} and bis-adduct molecules. Shape-complementary packing of convex and concave units in crystalline adducts of **1** and anthracene has been noted here and elsewhere [16a][19], while re-orientational mobility of **1** in crystals containing **1** is characteristically high [21]. It is thus likely that the implied specific stability of antipodal bis-adducts in combination with **1** is due to the packing of roughly shape-complementary molecular surfaces in a regular micro-crystalline environment (possibly in ordered linear stacks of the antipodal bis-adducts alternating with **1**). Indeed, the packing motif generated by the rigidly structured, concave and convex surfaces of cycloadducts of **1** and of anthracenes may not only be the source of unusual reactivity in the solid [15a], but may also be useful further for crystal design [22–24].

Conclusion. – The present work concerns a case of a remarkable self-assembly of fullerene bis-cycloadducts and may contribute to the current interest in solid-state transformations [15][22–24]. It provides an example in which a unique selectivity towards specific products is achieved. The needed high temperatures are tolerated here, although even at lower temperatures and in a (dilute) solution environment, the products are of limited stability. Our model considers arrays of stacked mono-adduct molecules as crucial reactive elements, which are well packed due to roughly shape-complementary concave/convex surface elements and which undergo topochemically controlled conversion to alternating stacks of C_{60} and its antipodal bis-adducts [15]. Further insights into the structure of crystalline mono- and bis-adducts of **1** and anthracenes and into the mechanistic aspects of the intriguingly simple and regioselective bis-functionalization reaction of C_{60} are desirable. The preparative interest in specific fullerene templates also mandates further investigations in the solid-state properties and transformations of adducts of anthracenes and fullerenes.

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Experimental Part

General. Chemicals: [5,6]fullerene-C_{60}-I_h (**1**), *Hoechst*, lab grade, 96% C_{60}, purified according to *Isaacs et al.* [25], or 99.5% from *Southern Chem. Group*, Texas; 1-methylanthracene (97%), *Aldrich Chem. Co.;* 2-methylanthracene, 9-methylanthracene, 9,10-dimethylanthracene, MeOH, CS_2 (for chromatography), hexane, pentane, all *Fluka purum*; anthracene, *Fluka puriss.*, scint. grade; 1,2-dichlorbenzene, CS_2, and $CHCl_3$ (for spectroscopy), *Fluka puriss.*; $CDCl_3$, 99.8% D, *Cambridge Isotopes*; 2,3,6,7-tetramethylanthracene, prepared according to *Bender* and *Müllen* [26]; 2,6-di(*tert*-butyl)anthracene, prepared according to *Fu* and *Harvey* [27]. Column chromatography (CC): silica gel *H* (for TLC), *Fluka*. TLC: *Polygramm-SIL G/UV-254* plates (CS_2/hexane 3 : 1). UV/VIS: *Hitachi U-3000*; $\lambda(\log \varepsilon)$ in nm. ^{1}H-NMR: *Varian 500 Unity plus*, 500 MHz, or *Varian 200 Gemini*, 200 MHz; δ ($CHCl_3$) 7.24. FAB-MS: *Finnigan MAT95*, positive-ion detection, CS/gun.

9′,9″10′,10″-Tetrahydrobis[9,10]ethanoanthra[11′,12′:1,9;11″,12″:52,60][5,6]fullerene-C_{60}-I_h (**3**). Finely powdered samples of crystalline **1** (30 mg, 41.6 µmol) and anthracene (14.8 mg, 83.2 µmol) were separately generated in a small mortar and then mixed homogeneously. The mixture was transferred into two melting-point capillaries, which were sealed. The sealed tubes were inserted into the heated bath of a *Büchi* melting-point apparatus and were heated at 240° for 60 min. The clean cooled melting-point capillaries were crushed mechanically (in a flask), and the dark solids were dissolved in CS_2 (*ca.* 40 ml) with the help of ultra sound. The soln. was concentrated to *ca.* 20 ml and then applied to CC (120 g of silica gel *H*, 55 × 4 cm colonne): three main components, *i.e.* 14 mg (46.7%) of **1**, 1.7 mg (4.5%) of **2**, and 19.6 mg (43.7%; 82% rel. to consumed **1**) of **3**. Dark solids which were identified by TLC, UV/VIS, ^{1}H-NMR, and FAB-MS [15][16a].

9′,9″,10′,10″-Tetrahydro-1′,1″-dimethyl[9,10]ethanoanthra[11′,12′:1,9;11″,12″:52,60][5,6]fullerene-C_{60}-I_h (**7**). As described for **3**, with **1** (40 mg, 55.1 µmol), and 1-methylanthracene (21.3 mg, 111 µmol) at 240° for 30 min. CC (210 g of silica gel *H*) gave 25.2 mg (64%) of **1**, 6.8 mg (13%) of **4**, and 14.0 mg (23%; 63% rel. to consumed **1**) of **7**. Dark solids. Fullerene **1** was analysed by TLC and UV/VIS, and **4** and **7** were identified by TLC, UV/VIS, ^{1}H-NMR, and FAB-MS.

Single crystals of **7**, suitable for X-ray analysis, were obtained by recrystallization of **7** from CS_2/$CHCl_3$ 10 : 1 at r.t. with protection from light: $C_{90}H_{12} \cdot 2\ CHCl_3$, M_r 1331.73, monoclinic, space group $P2_1/n$ (no. 14); $a = 9.8770(6)$, $b = 20.832(2)$, $c = 13.787(1)(2)$ Å; $\beta = 102.804(4)°$; $V = 2766.2(4)$ Å^3, $Z = 2$, $\rho_c = 1.599\ g \cdot cm^{-3}$, $\mu = 0.371\ mm^{-1}$; *Nonius Kappa CCD*, $\lambda = 0.71073$ Å (MoK_α); crystal dimensions 0.3 × 0.25 × 0.2 mm, *T* 223 K, 8904 reflections collected, 2575 unique reflections ($R_{int} = 0.0347$), 2115 reflections $I > 2\sigma(I)$; data reduction with DENZO-SMN [28], no absorption correction, structure solution with SHELXS86 [29], refinement on F^2 with SHELXL93 [30]. H-Atoms at C(31) and C(38) were found and were calculated and refined in the riding model with isotropic displacement parameters, H-atoms around the disordered Me group were omitted, the disordered positions of the Me group and the 1 : 1 disordered carbon C-atoms C(33), C(34), C(35), C(36), C(40), C(41), C(42), C(43), C(33a), C(34a), C(35a), C(36a), C(40a), C(41a), C(42a), C(43a) were refined isotropically, 460 parameters refined. *R* Values ($I > 2\sigma(I)$): $R_1 = 0.0666$, $wR_2 = 0.1584$; *R* values (all data): $R_1 = 0.0819$, $wR_2 = 0.1749$. Crystallographic data for the structures of **7** reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication no. CCDC 160919. Copies of the data can be obtained, free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code + (1223)336-033; e-mail: teched@chemcrys.cam.ac.uk).

9′,9″,10′,10″-Tetrahydro-9′,9″-dimethyl[9,10]ethanoanthra[11′,12′:1,9;11″,12″:52,60][5,6]fullerene-C_{60}-I_h (**8**). In an exploratory experiment analogous to the one reported for **3**, a homogeneous solid mixture of **1** (30 mg, 41.6 µmol) and 9-methyl anthracene (16.0 mg, 83.2 µmol) was heated in a sealed tube at 200° for 30 min. A small sample of the cooled mixture was quickly dissolved completely in CS_2 and analysed by TLC and UV/VIS which revealed significant amounts of **1**, the bis-adduct **8**, and 9-methylanthracene, besides traces of mono-adduct **5**. The remaining solid reaction mixture was then stirred in CS_2 (*ca.* 5 ml) under ultra sound. TLC and UV/VIS indicated the supernatant to contain largely the starting materials **1** and 9-methylanthracene and the dark solid (18.6 mg) mostly **5** and **8**. The solid was analysed by FAB-MS and 200-MHz ^{1}H-NMR [15b]. The latter indicated the solid to contain *ca.* 77 mol-% (*ca.* 13.6 μmol) of bis-adduct **8** (as a 1:1 mixture **8a**/**8b**), 16 mol-% of mono-adduct **5** (*ca.* 2.8 μmol), and 7 mol-% of 9-methylanthracene.

Crude 9′,9″,10′,10″-Tetrahydro-9′,9″,10′,10″-tetramethyl[9,10]ethanoanthra[11′,12′:1,9;11″,12″:52,60][5,6]-fullerene-C_{60}-I_h (**9**). In an exploratory experiment analogous to the one reported for **3**, a homogeneous solid mixture of crystalline **1** (90 mg, 124.9 μmol) and 9,10-dimethylanthracene (51.5 mg, 249.6 μmol) was heated in sealed tubes at 240° for 60 min. The cooled mixture was extracted first by *ca.* 5 ml, then by 3 ml of CS_2 under ultra sound (twice 1 min). TLC and UV/VIS indicated the supernatant to contain largely the starting materials **1** and 9,10-dimethylanthracene and the dark solid (50.0 mg) mostly **6** and **9**. A sample of the solid was completely dissolved in CS_2 and analysed by UV/VIS, FAB-MS, and 200-MHz ^{1}H-NMR, all recorded at r.t. [15b]. The latter revealed signals due to 41 mol-% (*ca.* 24.4 μmol) of the rapidly decomposing bis-adduct **9**, 43 mol-% (*ca.* 26 μmol) of the mono-adduct **6**, and 16 mol-% of 9,10-dimethylanthracene.

Control Experiment 1. In an experiment analogous to the one reported for **3**, a finely ground mixture of crystalline **1** (10 mg, 13.9 μmol) and 2-methylanthracene (5.3 mg, 27.6 μmol) was heated in sealed tubes at 240° for 30 min. The cooled mixture was dissolved in CS_2 by applying ultra sound. Analysis of the resulting soln. by TLC and UV/VIS revealed the presence of the starting materials **1** and 2-methylanthracene, $<10\%$ of a mono-adduct, and no other detectable products (TLC) derived from **1**.

Further Control Experiments. Heating, as described for **3**, in sealed tubes at 240° for 60 min a finely ground mixture of **1** (10 mg, 13.9 μmol) and 2,3,6,7-tetramethylanthracene (6.5 mg, 27.7 μmol) or 2,6-di(tert-butyl)anthracene (8.1 mg, 27.9 μmol), respectively, yielded mixtures which contained only the starting materials **1** and the corresponding anthracene, but no fullerene derivatives (by TLC and UV/VIS).

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