The Orthogonal (*e*,*e*,*e*)-Tris-Adduct of 9,10-Dimethylanthracene with C_{60}-Fullerene: A Hidden Cornerstone of Fullerene Chemistry

Preliminary Communication

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Tris(9′,10′-dimethyl[9,10]ethanoanthracene[11′,12′:1,9;11″,12″:16,17;11‴,12‴:30,31])[5,6]fullerene C_{60}, the orthogonal (*e*,*e*,*e*)-tris-adduct of C_{60} and 9,10-dimethylanthracene, was obtained from [4+2]-cycloaddition (*Diels–Alder* reaction) at room temperature. The thermally unstable orange red (*e*,*e*,*e*)-tris-adduct was purified by chromatography and was isolated in the form of red monoclinic crystals. Its C_3-symmetric addition pattern was established spectroscopically. Its structure could be further investigated by single crystal X-ray diffraction. The (*e*,*e*,*e*)-tris-adduct of C_{60} and 9,10-dimethylanthracene has earlier been suggested as intermediate and reversibly formed critical component in 'template directed' addition reactions of C_{60}. This previously elusive compound has now been isolated and structurally characterized.

Introduction. – The discovery of the fullerenes [1] and of an efficient method to produce substantial amounts of these spherical carbon molecules [2] has opened a new era of chemistry [1][3–5] and has paved the way to synthetic, spectroscopic, and structural studies [6]. One major goal of these studies concerned the exploration of methods to achieve specific exohedral modifications of the symmetric spherical C-skeleton of C_{60} (**1**) [7][8]. Among the methods developed to systematically functionalize C_{60} (**1**), cycloaddition reactions proved to be particularly useful, such as [1+2] cycloaddition (*Bingel* cyclopropanation) [9], [3+2] cycloaddition (*Prato* reactions) [10] and [4+2] cycloaddition (*Diels–Alder* reactions) [3][11–13]. A characteristic of the latter reaction is its inherent thermal reversibility and, as a consequence, often limited thermal stability of the fullerene-addition products [8][14–16]. The situation is different with the stable products of [1+2] and [3+2] cycloadditions, where the removal of an addend, if desirable, typically needs rather specific manipulations (such as, *e.g.*, electrochemical deprotection [17][18]). In other cases, the thermal reversibility was exploited to achieve reversible attachment of fullerenes to solid support [19].

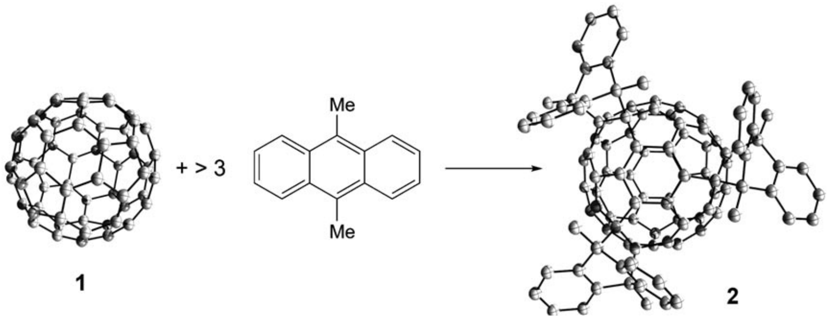
As the highly symmetrical C-sphere provided by the [5,6]fullerene **1** represents a unique basis for building up three dimensional molecular structures by multiple exohedral functionalization, particular attention was paid to the problem of regioselectivity in functionalization reactions [7][8]. The underlying need for regiocontrol has provoked extensive studies on *i*) the patterns of the inherent reactivity of [5,6]fullerene

C_{60} (**1**) and its mono-adducts [8][20], as well as complementary investigations on *ii*) how the reactions at the C-sphere can be directed further from outside [6][8]. Tether-directed remote functionalization [6][21] and topochemical control in the solid state [22] have opened new ways to achieve highly selective multiple addition reactions [8]. In addition, the use of protection-group strategies was developed to direct the incoming addends to the desired sites of attachment [8]. Thermally reversible [4+2] cycloaddition (or *Diels-Alder*) reactions of [5,6]fullerene C_{60} (**1**) with a variety of dienes and anthracenes were particularly valuable, in this context [23]. The antipodal (*trans-1*)-bisadduct of C_{60} and anthracene, (*trans-1*)-**1-A$_2$**, was used to efficiently obtain (*via* a mixed hexa-adduct and thermal removal of the protecting anthracene addends) symmetrical tetra-cyclopropanation products of C_{60} [24]. Another successful type of protection-group strategy, by 'template directed' multiple addition reaction, was developed by *Hirsch* and co-workers [25] and others [26]. These authors ascribed the efficient regioselective formation of hexa-adducts with a symmetrical addition pattern to the thermally reversible attachment of 9,10-dimethylanthracene [25] (or of 9,10-dimethoxyanthracene [26]). The suggested reversible *in situ* formation of the title compound, tris(9′,10′-dimethyl[9,10]ethanoanthracene[11′,12′:1,9;11″,12″:16,17;11‴,12‴:30,31])[5,6]fullerene C_{60} (**2**) was considered to direct the other (effectively irreversibly bound) addends at the desired sites [25], so that, typically, a good yield of hexa-addition products with pseudo-octahedral addition pattern was achieved [27]. However, so far, the (*e*,*e*,*e*)-trisadduct **2** has been elusive and has remained uncharacterized. Here, we report the preparation and structure analysis of **2**.

In solution, the [5,6]fullerene C_{60} (**1**) and 9,10-dimethylanthracene react readily at room temperature to give, first, the mono-adduct **1-A$_1$**. By inducing it to crystallize out of the reaction mixture, mono-adduct **1-A$_1$** was obtained selectively and in 74% yield [23]. Thermal decomposition of solid mono-adduct **1-A$_1$** was shown to be an efficient method to prepare the antipodal bisadduct (*trans-1*)-**1-A$_2$** of C_{60} and 9,10-dimethylanthracene [23]. However, further reaction in solution of the mono-adduct **1-A$_1$** with 9,10-dimethylanthracene also occurs readily to give a mixture of higher adducts, *i.e.*, mainly bisadducts and trisadducts [28]. This type of reversible addition reaction has been suggested to provide selectivity in 'template-directed' multiple-addition reactions, where the elusive tris-adduct **2** (with an orthogonal (or *e*,*e*,*e*-) addition pattern of the [5,6]fullerene C_{60} (**1**) and of 9,10-dimethylanthracene) was given a crucial role as a 'template' [25]. The labile tris-adduct **2** was obtained here from (conventional) reaction in concentrated solution at room temperature, chromatographic separation of the reaction mixture, and crystallization (see *Scheme*).

Results and Discussion. – At room temperature, C_{60} (**1**) and 9,10-dimetylanthracene reacted readily in concentrated solution [23][28]. Within 2 h, bis- and tris-adducts **1-A$_2$** and **1-A$_3$**, respectively, were formed from **1** and a twofold excess of 9,10-dimetylanthracene. Workup of the reaction mixture and chromatography on silica gel *H* with CS_2/hexane 3:1 as eluent provided the characteristically orange-colored fraction of the (*e*,*e*,*e*)-trisadduct **2** (=(*e*,*e*,*e*)-**1-A$_3$**) as the most polar of several fractions of (non-identified) bis- and tris-adducts. When the orange chromatographic fraction was stored overnight at 0°, *ca.* 10.2 mg (9%) of dark orange-red crystals of **2** directly separated. Some of the crystals were selected for crystallographic analysis, and the remaining solid

Scheme. *Formation of the (*e,e,e*)-Tris-Adduct* **2** *by Cycloaddition of 9,10-Dimethylanthracene and* C_{60} (**1**)



was dried. A rapidly recorded UV/VIS spectrum of a solution of **2** in $CHCl_3$ showed a broad absorption maximum at 447 nm and a shoulder at 565 nm (see *Fig. 1*). The same spectral features were also observed in the more stable tris-orthogonal (or *e*,*e*,*e*) trisadduct of anthracene with [5,6]fullerene C_{60} (**1**) [29]. In solution and at ambient temperature, the tris-adduct **2** decomposed within minutes (first to the 'equatorial' *e*-bisadduct *e*-**1-A$_2$** and then to the monoadduct **1-A$_1$**). In the crystalline state and at room temperature, the red-orange (*e*,*e*,*e*)-trisadduct **2** was stable.

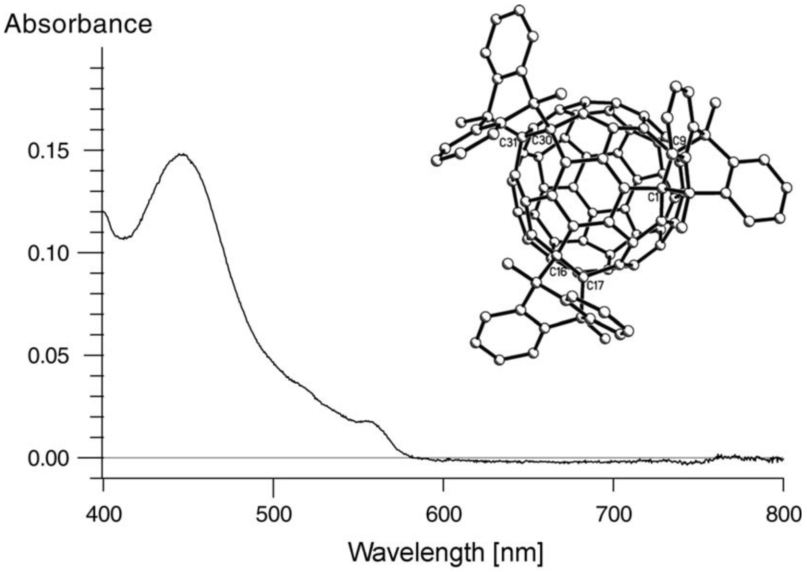


Fig. 1. *Visible long-wavelength section of absorbance spectrum of the tris-adduct* **2** *in* $CHCl_3$ (c = 0.152 mM)

The molecular formula of the orange compound was deduced from its FAB mass spectrum, which exhibited a pseudo-molecular ion ($[M+H]^+$) at m/z 1339.36, corresponding to a molecular formula of $C_{108}H_{42}$ and a prominent fragment ion at m/z 1133.2 for $[M+H-C_{16}H_{14}]^+$. In a 200-MHz ^{1}H-NMR spectrum of **2** (in CS_2/

$CDCl_3$ 3 : 1), two *singlet*s for Me groups at 1.77 and 2.41 ppm, and a *multiplet* at low field for aromatic H-atoms were observed (after 5 min, also other signals became significant, such as a *singlet* at 3.10 ppm, due to decomposition of **2** and formation of 9,10-dimethylanthracene). The original spectrum indicated the tris-adduct **2** to have C_3-symmetry.

From the solution in CS_2/hexane 3 : 1, orange-red monoclinic crystals of the tris-adduct **2** separated at *ca.* 0°, some of which were suitable for analysis by X-ray diffraction. The tris-orthogonal trisadduct **2** crystallized in the space group *P*2(1)/*n*. The elemental cell contained four molecules of **2** and twelve molecules of CS_2. The crystal structure (see *Fig. 2*) confirmed the unique C_3-symmetric addition pattern, derived from the NMR spectra. Attachment of the three anthracene addends occurs through long C–C bonds (161.6 pm) and generates six saturated C-centers on the fullerene sphere. These cluster around one six-membered ring of the remaining unsaturated fullerene moiety. This six-membered ring has shorter C–C bonds (138.3 and 142.4 pm), with less bond-length alternation, and its C-centers are less pyramidal (sum of bond angles: 354.4° at C(2), 349.1° at C(3); see *Fig. 2*) than in the corresponding ring at the other pole of the fullerene sphere (with C–C bonds of 139.7 and 144.7 pm, and with a uniform and rather smaller sum of bond angles of *ca.* 347.7°).

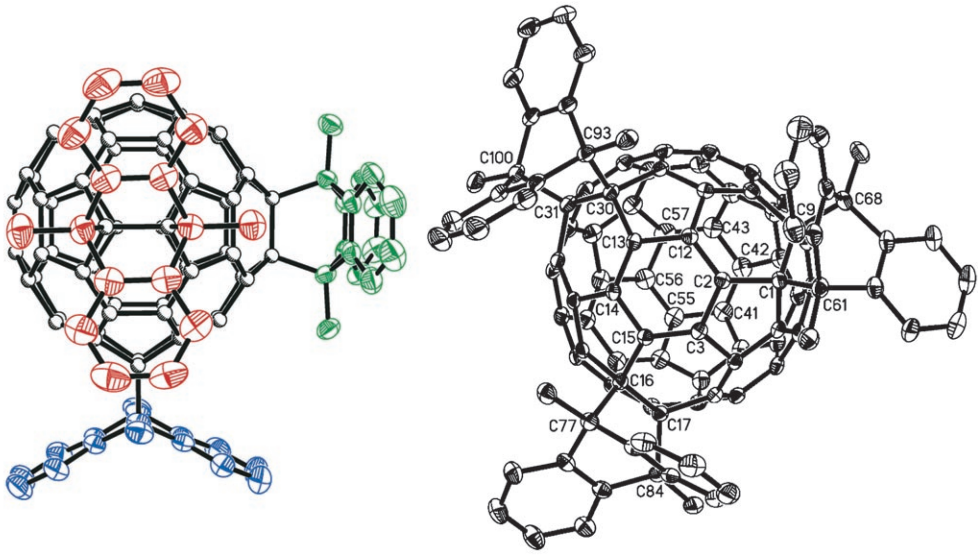


Fig. 2. *Molecular structure of the* (e,e,e)*-tris-adduct* **2** *in the crystal according to X-ray analysis. Left:* view down on a site of attachment; *right:* view along the three-fold symmetry axis.

In the crystal, tris-adduct **2** was observed to be organized in layers in three dimensions (see *Fig. 3*), but the molecules did not show 'shape-complementary' intermolecular contacts. Shape-complementary, regular intermolecular contacts between 'concave' [4 + 2] cycloaddends and the 'convex' fullerene sphere of a neighbor [5,6]fullerene molecule have been observed in a variety of crystal structures with C_{60}: *e.g.*, in the [4 + 2] cycloadducts of **1** with cyclohexa-1,3-diene [22], in mono- and bis-

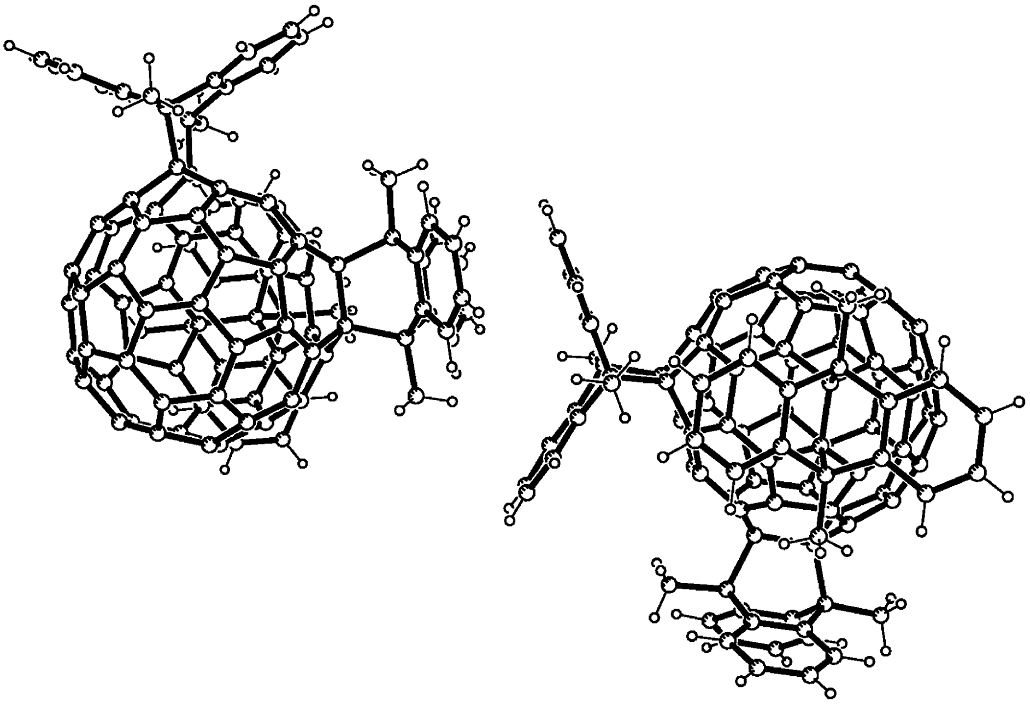


Fig. 3. *Crystal packing and motif of an intermolecular contact of the (*e,e,e*)-tris-adduct* **2** *in the crystal*

adducts with anthracene [30][31], and in cocrystals of C_{60} and triptycene [32] and with biconcave porphyrins [33].

Conclusions. – Exohedral addition products of [5,6]fullerene C_{60} (**1**) with a regular multiple-addition pattern have systematically been prepared by tether-directed functionalization, including a series of tris-addition products [34][35]. Cyclopropanation has turned out to be particularly useful for obtaining thermally stable tris-adducts of **1** with (*e*,*e*,*e*)-addition pattern [36][37]. In some of these reactions, the reversible cycloaddition of 9,10-dimethylanthracene was often inferred to be crucial to achieve selective template-directed addition [37]. In the present work, it was possible to isolate and to characterize spectroscopically the thermally labile (*e*,*e*,*e*)-trisadduct **2** from threefold [4+2] cycloaddition of C_{60} and 9,10-dimethylanthracene in solution. The trisadduct **2** crystallized readily, and the molecular structure of this previously elusive, but crucial intermediate in 'template-directed' multiple addition reactions of **1** was also characterized by means of X-ray analysis. Clearly, the readiness of certain regularly structured and rigid addition products of C_{60} (**1**) to crystallize [30][31] is a particular asset for the characterization of thermally labile addition products of C_{60}.

Experimental Part

General. [5,6]Fullerene C_{60}, *Hoechst*, lab grade, 96% C_{60}, purified according to [38] or 99.5% from *Southern Chem. Group*, Texas. 9,10-Dimethylanthracene, MeOH, CS_2 (for chromatography), hexane, all *Fluka purum.* CS_2 and $CHCl_3$ (for spectroscopy), *Fluka puriss.*; $CDCl_3$, 99.8% D, *Cambridge Isotopes.* TLC: *POLYGRAMM SIL G/UV 254* plates (CS_2/hexane 3 : 1). Column chromatography (CC): silica gel *H* (for TLC), *Fluka*. UV/VIS Spectroscopy: *Hitachi U-3000*, in λ [nm] (log ε). ^{1}H-NMR: *Varian Gemini 200* (200 MHz) apparatus; in δ [ppm] with $\delta(CHCl_3) = 7.19$ as reference. FAB-MS: *Finnigan MAT95*, in *m*/*z* ([%]), positive-ion detection, Cs-gun.

Synthesis of Tris(9′,10′-dimethyl[9,10]ethanoanthracene[11′,12′:1,9;11″,12″:16,17;11‴,12‴:30,31])-[5,6]fullerene C_{60} (**2**). In 5 ml of CS_2, 60 mg of C_{60} (0.085 mmol) and 34.5 mg of 9,10-dimethylanthrancene (0.17 mmol, 2 mol-equiv.) were dissolved with the aid of ultrasonication. The mixture was protected from daylight and was stored at r.t. for 2 h. The product mixture then was applied to a chromatography column (130 g SiO_2 *H*, $\varnothing = 5$ cm, $l = 30$ cm), and it was separated with CS_2/hexane 3 : 1 as eluent. After elution of small amounts of starting materials (9,10-dimethylanthracene and C_{60}), of several dark colored fractions (mono-adducts, bis-adducts, and other tris-adducts), a fraction of the orange-red **2** was eluted. The soln. containing **2** in CS_2/hexane *ca.* 3 : 1 was stored in a refrigerator for 24 h, when red crystals of the trisadduct **2** separated. Several of the monoclinic crystals were removed for the

Table. *Crystal Data and Details of the Structure Refinement for the (*e,e,e*)-Tris-Adduct* **2**

Empirical formula	$C_{108}H_{42} \cdot 3\ CS_2$
Formula weight	1567.81
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$ (No. 14)
Unit cell dimensions	$a = 12.8202(3)$ Å $b = 25.6072(7)$ Å $c = 21.1000(4)$ Å $\alpha = 90°$ $\beta = 90.118(2)°$ $\gamma = 90°$
Volume	6926.9(3) Å^3
Z	4
Density (calculated)	1.503 Mg/m^3
Absorption coefficient	0.260 mm^{-1}
F(000)	3216
Crystal size	$0.32 \times 0.12 \times 0.09$ mm^3
Theta range (for data collection)	2.96 to 22.50°.
Index ranges	$0 \le h \le 13$, $0 \le k \le 27$, $-22 \le l \le 22$
Reflections collected	16220
Independent reflections	8867 [R(int) = 0.0362]
Reflections [$I > 2\sigma(I)$]	6372
Completeness to $\theta = 22.50°$	97.9%
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8867/0/1061
Goodness-of-fit on F^2	1.059
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0631$, $wR_2 = 0.1587$
R Indices (all data)	$R_1 = 0.0923$, $wR_2 = 0.1745$
Extinction coefficient	0.0030(5)
Largest diff. peak and hole	0.537 and -0.769 e · Å^{-3}

crystal structure analysis. The remaining sample was dried to give 10.03 mg (0.075 mmol, 8.8% yield) of **2**, to be analyzed as follows (due to the lack of stability, spectra were typically recorded within 3 min after dissolution of the crystalline samples): TLC (SiO_2 *H*; CS_2/hexane 3 : 1): R_f 0.20. UV/VIS ($CHCl_3$, $1.52 \cdot 10^{-4}$ M): 554 (3.02), 513 (sh, 2.25), 447 (3.80), 380 (sh, 3.93). ^{1}H-NMR (200 MHz, $CS_2/CDCl_3$ 3 : 1): 1.77 (*s*, 9 H, H−C(9′)); 2.41 (*s*, 9 H, H−C(10′)); 7.25–7.29 (*m*, 24 H, H−C(1′), H−C(2′), H−C(3′), H−C(4′), H−C(5′), H−C(6′), H−C(7′), H−C(8′)). FAB-MS (NOBA matrix): 1340.45 (10), 1339.36 (11, $[M+1]^+$), 1338.18 (3), 1133.21 (10, $[M+1-C_{16}H_{14}]^+$), 1132.18 (8), 927.06 (8), 720.92 (100, $[C_{60}+1]^+$).

X-Ray Crystal-Structure Analysis of **2**. The data collection was performed at 295 K on a *Nonius Kappa* CCD equipped with graphite-monochromatized MoK_α radiation ($\lambda = 71.073$ pm) and a nominal crystal-to-area-detector distance of 36 mm. Intensities were integrated using DENZO and scaled with SCALEPACK [39]. The structure was solved with direct methods (SHELXS97) and refined against F^2 (SHELX97) [40]. All non-H-atoms were refined with anisotropic displacement parameters. Positions of H-atoms were calculated using a riding model (for details, see the *Table*).

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