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Diels-Alder Reactions of the [60]Fullerene [a]

Functionalizing A Carbon Sphere With Flexibly and With Rigidly Bound Addends

Bernhard Kräutler* & Josef Maynollo

Institute of Organic Chemistry, University of Innsbruck, A-6020 Innsbruck, Austria

Abstract: The regioselective functionalization of the [60]fullerene (**1**) (buckminsterfullerene) by way of [4+2]-cycloaddition reactions (Diels-Alder reactions) has given synthetic access to exohedrally derivatized fullerenes, with either flexibly or rigidly bound addends. The binding of the addends to the central carbon sphere can be made effectively irreversible by subsequent addition reactions at their double bond.

INTRODUCTION

The discovery of the fullerenes about 10 years ago [1] and of a method for their preparation in macroscopic quantities, five years later [2], has opened research on the exo- or endohedral chemical reactivity of carbon spheres [3,4]. The exploration of the reactivity in addition reactions of the regularly structured and unsaturated carbon networks of the fullerenes deserves special interest for the purpose of the preparation of specific fullerene derivatives by regiocontrolled exohedral functionalization [4]. In the last five years the synthesis of uniformly exohedrally monofunctionalized fullerene derivatives in preparative quantities has been explored with success [4] by a variety of addition reactions [5,6], most notably by a range of cycloaddition reactions [7,8] and by organometallic addition reactions [9].

A remarkable selectivity of the [60]fullerene (**1**) in specific highly regiocontrolled multiple addition reactions was revealed by the crystal structure of highly symmetric organometallic hexaaddition products [9a]. More recently then, the preparation of specific multiply functionalized derivatives of **1** with organic addends has been taken up in several chemical research laboratories [10], exploiting the noted regioselectivity of the cycloaddition step, which occurs at (6,6)-bonds of the [60]fullerene [4].

The synthetically powerful approach to functionalization of a multiunsaturated carbon surface, such as that of **1**, via the Diels-Alder reaction, originally was considered to be problematic, due to the reversibility of this thermal [4+2]-cycloaddition reaction [8a]. Accordingly, early examples of the monofunctionalization of the

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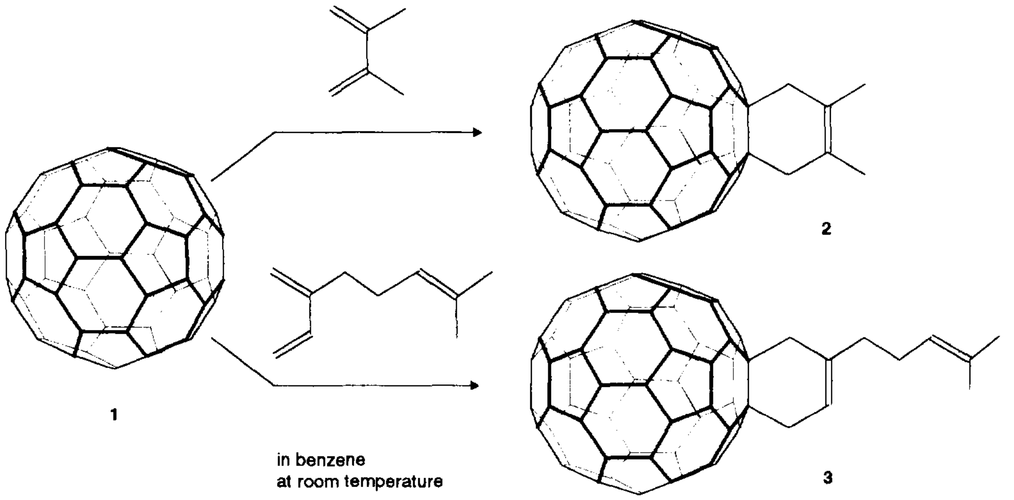
[a] Dedicated to Prof. Dr. Richard Neidlein on the occasion of his 65th birthday

[60]fullerene (**1**) by this route concern the use of o-xylylene-derivatives as dienes [8]. This led to fullerene derivatives with flexible addends at the (6,6)-bonds of **1**, as revealed by the temperature dependence of ^{1}H-NMR spectra of the Diels-Alder products [8b]. The synthesis of several specifically functionalized derivatives of **1** has been achieved in this way, such as of tetraaza-porphyrin [8d] and of steroid derivatives of **1** [8e].

In contrast, from addition of the cyclic dienes cyclopentadiene [11a,b] and pentamethyl-cyclopentadiene [11c] to the [60]fullerene (**1**), derivatives of this carbon sphere with rigidly bound addends at the (6,6)-bonds were accessible in good yields. Saturation of the addend by hydrogenation of the remaining double bond was achieved, so that the eventual thermal reversibility of the cycloaddition reaction could be undercut effectively [11a]. In fact, little still is known on the thermal stability of these and other Diels-Alder adducts of **1**: except for the cyclopentadiene monoadduct [11d], only qualititive information on the thermally induced cleavage (retro-Diels-Alder reaction) of [4+2]-cycloadducts is available [11e].

The high reactivity of the [60]fullerene (**1**) as dienophile with unactivated dienes, such as 2,3-dimethylbutadiene, the monoterpene myrcene and similar dienes was reported from this and other laboratories in 1993 [12]. The cycloaddition products 1,2[2',3'-dimethyl-2'-butene-1',4'-diyl]-1,2-dihydro-[60]fullerene (**2**) and 1,2[2'-(4"-methyl-3"-pentenyl)-2'-butene-1',4'-diyl]-1,2-dihydro-[60]fullerene (**3**) were found to form at room temperature without sign of thermal reversibility [12a]. The high apparent symmetry of **2** and **3**, indicated in the ^{1}H-NMR spectra at room temperature (as C_{2v} and as C_s, respectively), was compatible with a relatively low barrier of interconversion of the flexibly bound, but presumably nonplanar addends (see below).



Scheme 1

More recently, with the formation in a one-pot reaction of the highly symmetric hexaaddition product **4** from 2,3-dimethyl-butadiene and the [60]fullerene **1** the remarkable tendency of the carbon sphere **1** to form regularly structured multiple addition products ("radiolarenes") could be demonstrated in this group[10d].

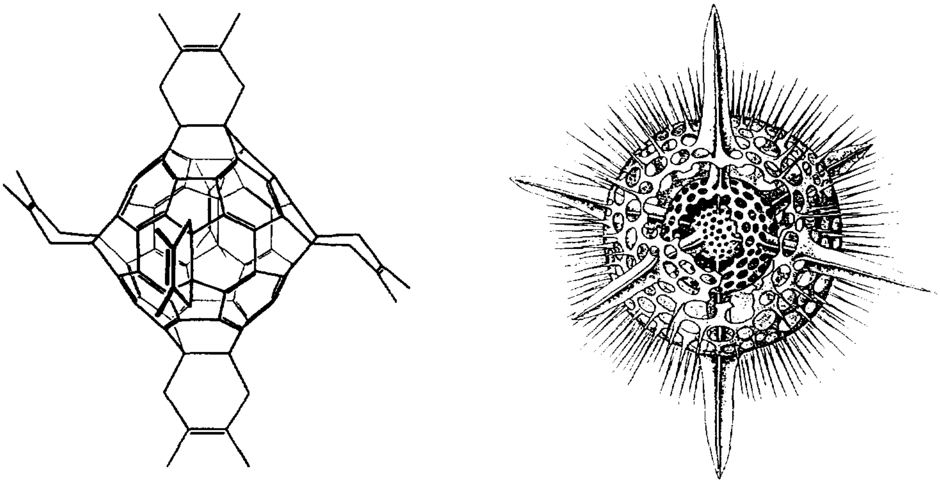
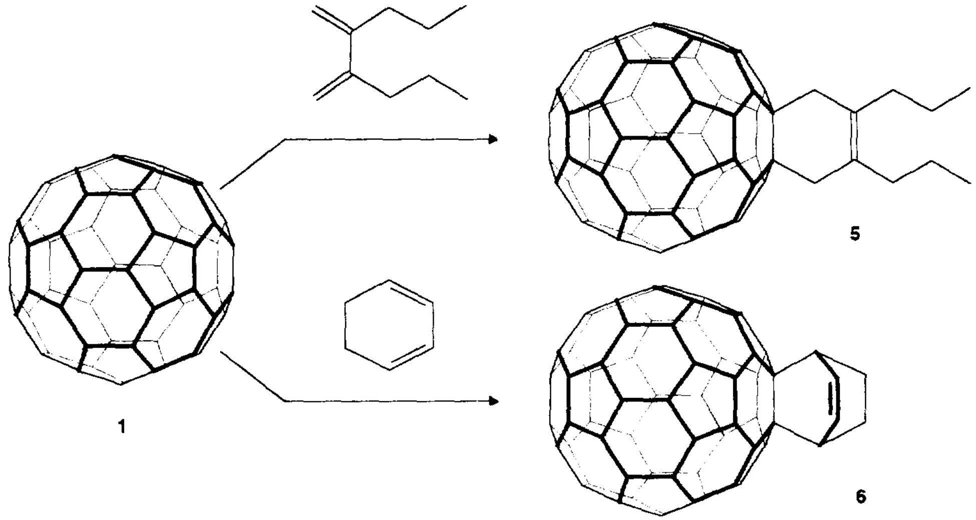


Figure 1: Model of the hexaaddition product **4** and of the skeleton of the structure of the radiolarium *Hexacontium asteracanthion* (right) according to Haeckel (ref. [13])

Here we report on further studies on the structure of **4** and on further monoaddition products of 1,3-dienes with **1**, with flexibly and with rigidly bound addends.

RESULTS AND DISCUSSION

Due to the low solubility of the Diels-Alder product **2** in solvents used for NMR-spectroscopy, its spectroscopic analysis earlier had been complicated. An alternative, that has turned out to have more practical solubility properties, is the bishomologuous 1,2[2',3'-dipropyl-2'-butene-1',4'-diyl]-1,2-dihydro-[60]fullerene (**5**), meanwhile obtained from cycloaddition of **1** and 2,3-dipropylbutadiene (see Scheme 2).



Scheme 2

The ^{1}H- and ^{13}C-NMR spectra of a solution of 5 in $CS_2/CDCl_3$ (4:2), measured at room temperature, are compatible with an effective C_{2v} symmetry of 5. However, at temperatures below −10° C the signal pattern becomes more complex, due to splitting of diastereotopic geminal protons into AB-systems. A coalescence temperature of 269 K indicates an activation barrier of 12,4 kcal/mol for the conformational process involving the cyclohexene-like substituent.

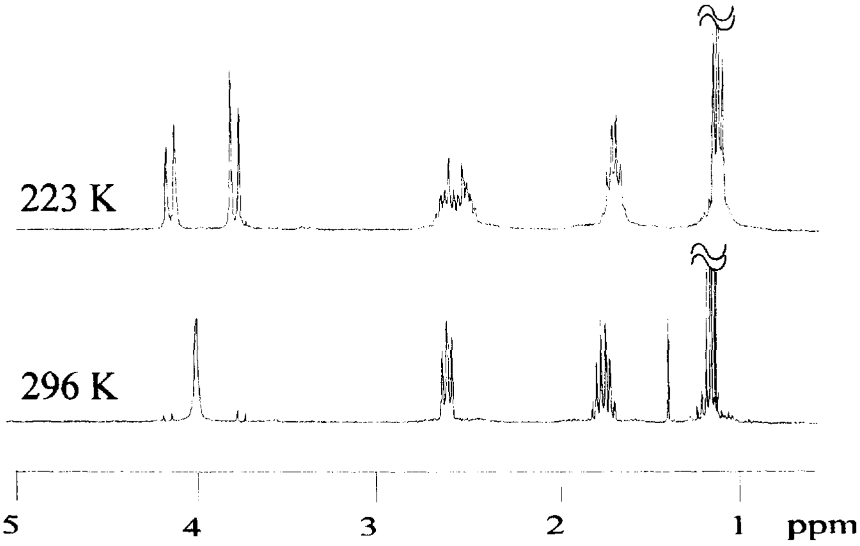


Figure 2: 300 MHz ^{1}H -NMR-spectra of 5 in CS_2:$CDCl_3$ (4:2) at 296 K (bottom) and 223 K (top)

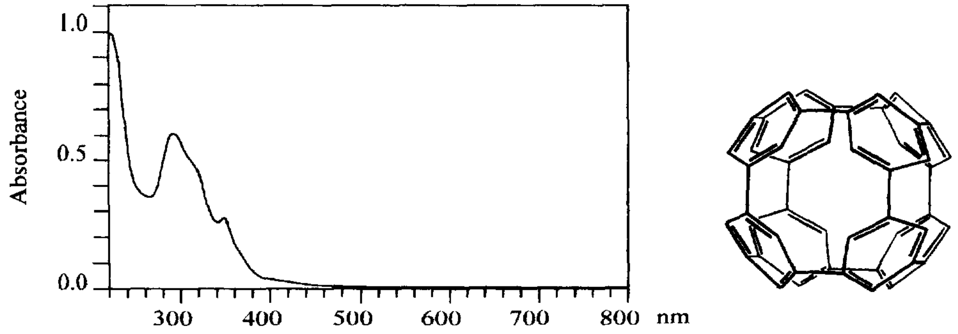


Figure 3: UV/VIS absorption-spectrum of the hexaadduct **4** (c = 3,7.10^{-4} M in CH_2Cl_2, d = 0,1 cm) and structure of the residual chromophore of **4**

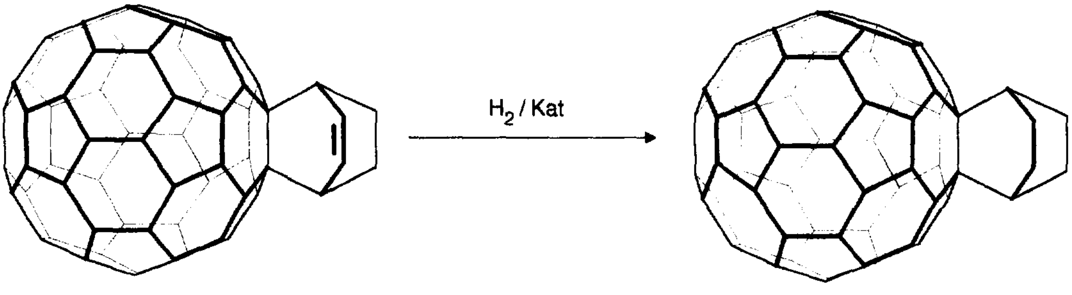
For the hexaaddition product **4** from reaction of **1** with an excess of 2,3-dimethylbutadiene, the room temperature NMR-spectra were compatible with an effective T_h-symmetry. However, in agreement with expectations concerning the nonplanar nature of the bridging buteno-groups, the ^{1}H-NMR spectra of a solution of **4** in $CDCl_3$ proved to be temperature dependent: the (broad) singlet at 3.99 ppm of the allylic methylene hydrogens in the spectrum measured at room temperature split into a poorly resolved AB-system at 2,7/3,0 ppm at 233 K, with the coalescence occurring in a temperature range near 253 K. From this value, a mean activation barrier of ca. 12 kcal/mol can be estimated, similar to that calculated from the spectra of the monoadduct **5**.

Taking into account the indicated nonplanar minimum energy structure of the 2-buteno-addends, the hexaadduct **4** correspondingly occurs in a series of slowly interconverting conformational isomers, most of which actually are chiral and even asymmetric. In this way, the hexaadduct **4**, which exhibits spectral characteristics at room temperature of a highly symmetric and ordered object, from low temperature studies is revealed to exhibit a comparatively complex behaviour: in this hydrocarbon, a cyclophane-like center spans a rigid and regular core, derived from the carbon sphere **1**, on which six addends provide a periphery made up of conformationally flexible, substituted six-membered rings.

The spectral behaviour of **5** allows it characterization as a product of a [4+2]-cycloaddition of the symmetric butadiene at one of the (6,6)-bonds of **1** whose nonplanar, boat shaped addend rapidly conformationally interconverts the positions of the diastereotopic hydrogens at the allylic methylene carbons, similar to the situation (but with somewhat lower barriers to interconversion) as observed earlier with the o-xylylene adducts to **1** [8b]. The mass spectral data of **5** are consistent with a molecular formula of $C_{70}H_{18}$ and its UV/VIS-spectrum exhibits absorption maxima at 435 nm and 708 nm, characteristic of (6,6)-cycloadducts of **1** [8b,8c,12].

The addition of cyclohexadiene to the dienophile **1** also occurs readily (at room temperature), to give the (6,6)-monoadduct **6** (1,2-{1',2',3',4'-tetrahydro-[1',4']epicyclohexa}-[60]fullerene) in 30% yield (see Scheme 2). The ^1H- and ^{13}C-NMR spectra of a solution of **6** in $CS_2/CDCl_3$ (4:2), now are compatible, as expected, with an adduct with C_s-symmetry and bearing a rigidly bound addend. Similar to the situation in the cyclopentadiene cycloadduct of **1** [11a,b], the hydrogen signals of **6** are all shifted to low field, when compared, e.g. to those of cyclohexene.

Catalytic dihydrogenation of **6** can be achieved at room temperature to occur exclusively at the (C=C)-double bond of the addend and to furnish the adduct 7, with a saturated addend (see Scheme 3) and therefore prevented from undergoing fragmentation by a retro Diels-Alder reaction. The NMR-spectra of the adduct 7 (1,2-{1',2',3',4',5',6'-hexahydro-[1',4']epicyclohexa}-[60]fullerene) reflect the increased overall symmetry (when going from **6** to 7), giving rise to just 3 signals (of 3 sets of chemically equivalent hydrogens) in the ^1H-NMR spectrum of the C_{2v}-symmetric 7. Likewise, its H-decoupled ^{13}C-NMR spectrum consists of 16 lowfield and 3 high field signals.



6 **7**

Scheme 3

The UV/VIS-spectrum of 7 shows the characteristics of that of the (6,6)-cycloaddition products and differs hardly from that of its hydrogenation precursor **6**, providing excellent evidence for the lack of hydrogenation at the fullerene core. The FAB-MS spectrum of 7 exhibits a strong signal for its molecular ion $(M+1)^+$ at m/z = 803 (34 %), whose accurate mass determination confirms its expected composition as that of $C_{66}H_{11}$.

CONCLUSION AND OUTLOOK

The [60]fullerene (**1**) is a powerful dienophile and of similar reactivity towards simple dienes, as maleic anhydride [12a]. Diels-Alder reactions allow the preparation in good yields of a variety of derivatives of **1**, in which the addends may be flexibly or rigidly bound to the (6,6)-bonds of the central sphere. Multiple additions of suitable dienes can occur with considerable selectivity with respect to the potential sites of addition. In this way highly symmetric hexaaddition products (with T_h or quasi T_h symmetry) can be obtained in one-pot reactions. Such hexaaddition products appear to contain relatively stable novel cyclophane structures comprising eight symmetrically arranged benzene rings, and further cycloaddition steps are thermodynamically and kinetically unlikely.

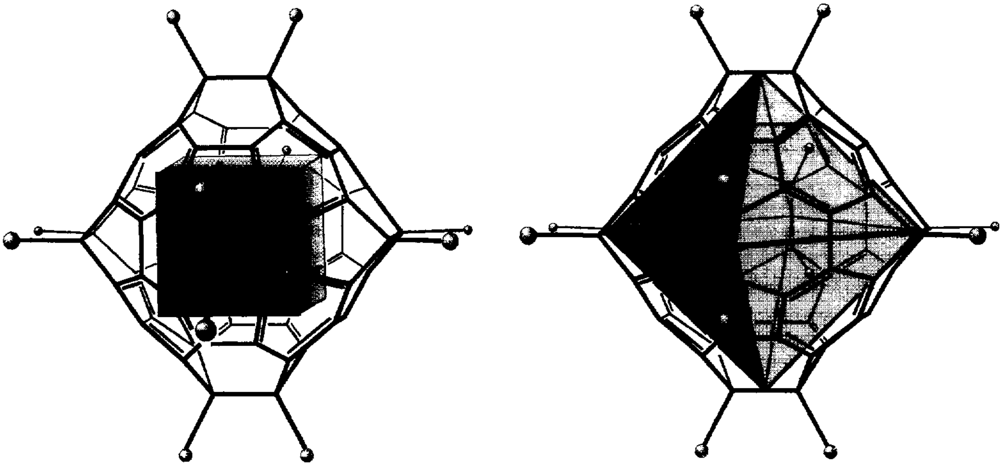


Figure 4: Superposition of the framework of T_h-symmetric adducts (such as **4**) with a cube (left) and with an octahedron (right)

The three-dimensional build-up of the carbon sphere **1** thus provides a unique basis for the design and for the preparation of molecular structures with spherical cores and exhibiting highly esthetic symmetries. In this respect, the variety of forms offered by the structures of the carbon skeletons of radiolaria [13] may be natural models. Symmetrically multifunctionalized fullerenes, from exohedral, covalent functionalisation via the Diels-Alder reaction, in turn, may be of use as novel, three dimensionally structured, rigid or flexible, polyunsaturated molecular building blocks, possibly providing a basis for the build up of materials with unusual solid state properties.

EXPERIMENTAL PART

Solvents and reagents: Benzene, *Fluka puriss. p.a.*; carbon disulfide, *Fluka purum*; cyclohexa-1,3-diene, *Fluka purum*; 1,2-dichlorobenzene, *Fluka purum*; dichloromethane, *Fluka puriss. p.a.*; fullerene C_{60} (**1**), *Hoechst Lab-Grade*, purified according to ref [14]; hexane, *Fluka puriss. pa.*; hexane fraction, *Fluka purum*; pentane fraction, *Fluka purum*; platinum(IV)oxide hydrate ("Adams-catalyst"), *Fluka puriss. p.a.*; 1,1,2,2-tetrachloroethane, *Fluka purum*; toluene, *Fluka puriss.p.a.*; tris(acetylacetonato)Cr(III) ("Cr(III)(acac)$_3$"), *ICN Biomedicals Inc.*; aluminium oxide, *Macherey-Nagel Act. I, neutral.* TLC: silica gel plates, *Macherey-Nagel Art.-Nr.: 805021*, aluminium oxide-plates, *Macherey-Nagel Art.-Nr.: 802021.*

^{1}H-NMR: 300.14 MHz, *Bruker AM-300*, $CS_2/CDCl_3$ 4:2 v:v ($\delta(CHCl_3)$=7.26 ppm), ^{13}C-NMR 75.74 MHz *Bruker AM-300*, $CS_2/CDCl_3$ 4:2 v:v, ($\delta(CS_2)$=192.8 ppm), ^{13}C-NMR 125.7 MHz *Varian Unity* 500 CS_2/CD_3COCD_3 9:1 v:v ($\delta(CS_2)$=192.8 ppm). FT-IR: *Mattson FTIR 3000* (KBr cm^{-1}). UV/VIS: *Hitachi U-3000, HP8452A* (1,1,2,2-tetrachloroethane λ_{max}nm(log ε)) FAB-MS: *Finnigan MAT-95*, NOBA (3-nitrobenzyl alcohol) as matrix, Cs, positive ion detection (m/z (%)).

Preparation of 1,2[2',3'-dipropyl-2'-butene-1',4'-diyl]-1,2-dihydro-[60]fullerene (5): In 30 ml benzene 30 mg **1** (0.041 mmol) and 28.3 mg 2,3-dipropyl-1,3-butadiene (0.205 mmol, 5mequ, prepared according to ref. [15]) were dissolved and the solution was heated under reflux for 14 hours with protection from light and under Ar. The reaction mixture was absorbed on 10g aluminium oxide and seperated on a column of 50g aluminium oxide using hexane as eluent. After complete elution of **1**, **5** was eluted with hexane/dichloromethane 8:2. 12.3 mg of **1** were recovered and 22.2 mg **5** were isolated. Recrystallization of the latter from carbon disulfide/hexane gave 18.3 mg pure **5** (51.4 % yield).

R_f (alox, hexane): 0.78. - ^{1}H-NMR: T= 296K: 1.15(t, J=7.4 Hz, 6H), 1.74(m, J=7.7 Hz, 4H), 2.61(t, J=7.7 Hz, 4H), 3.99(s, 4H). T= 223K: 1.10(t, J=7.4 Hz, 6H), 1.67(m, J=7.4 Hz, 4H), 2.54 (m, 4H), 3.75/4.11 (AB-system, J= 13.7 Hz, 4H) .- ^{13}C-NMR (75,74 MHz): 14.45, 22.45, 35.02, 44.76, 66.60, 135.56, 135.77, 139.95, 141.39, 141.83, 142.15, 142.36, 142.75, 142.85, 144.51, 145.21, 145.32, 145.51, 145.98, 146.25, 147.37, 157.01 .- FT-IR (3%): 2951(m), 2922(m), 2862(m), 1512(m), 1460(m), 1450(m), 1427(m), 526(s).- UV/VIS ($6.5x10^{-4}$M) 708 (2.32), 640 sh (2.39), 435 (3.39).- FAB-MS: 861 (17), 860 (31), 859 ((M+1)$^+$, 22), 721 ((C_{60}+1)$^+$,100), etc.

Preparation of 1,2-{1',2',3',4'-tetrahydro-[1',4']epicyclohexa}-[60]fullerene (6): In 25 ml toluene 50 mg **1** (0.069 mol) and 27.7 mg cyclohexa-1,3-diene (0.345 mmol, 5 mequ) were dissolved and the solution was heated to 90°C for two hours with protection from light and under Ar. The reaction mixture was absorbed on 12g aluminium oxide and separated on a column of 150g aluminium oxide using hexane/toluene 19:1. After complete elution of **1**, **6** was eluted with hexane/toluene 1:1. 24.2 mg of **1** were recovered and 25.5 mg **6** were isolated. Recrystallisation of the latter from 1,2-dichlorobenzene/pentane-fraction gave 17.0 mg pure **6** (30.3 % yield).

R_f (alox, hexane): 0.58. - ^{1}H-NMR: 2.26 (m, 2H), 3.20 (m, 2H), 4.12 (m, 2H), 7.31 (m, 2H). ^{13}C-NMR (75,74 MHz) (2,1x10^{-2}M, 1.4 mequ Cr(III)(acac)$_3$):25.97, 44.12, 70.39, 135.70, 136.63, 137.28, 140.30, 140.47, 141.97, 141.99, 142.17, 142.25, 142.38, 142.68, 142.90, 142.95, 143.43, 144.96, 145.65, 145.74, 145.84, 145.87, 146.10, 146.37, 146.46, 146.49, 146.65, 146.76, 147.79, 156.39, 156.91. UV/VIS (6.2x10^{-4} M): 710 (2.56), 640 sh(2.56), 605 sh(2.76), 540 sh(2.96), 480 sh(3.16), 436 (3.54), 320 sh(4.47), 305 sh(4.51). FAB-MS: 802 (23), 801 ((M+1)$^+$, 37), 800 (M$^+$, 30), 721 ((C_{60}+1)$^+$, 100), 720 (91), etc.

Preparation of 1,2-{1',2',3',4',5',6'-hexahydro-[1',4']epicyclohexa}-[60] fullerene (7): In 105 ml toluene 15.0 mg of **6** were dissolved. After addition of 42 mg of platinum(IV)oxide-hydrate the mixture was hydrogenated at 40 psi at room temperature for 40 minutes. The solid was removed by filtration and the solvent was evaporated. The product was chromatographed on a short column of silica. Precipitation from carbon disulfide with hexane gave 7.2 mg **7** (47% yield).

R_f (silica, hexane): 0.57. - ^{1}H-NMR: 2.55 (m,4H), 3.18 (m,6H).- ^{13}C-NMR (125,7 MHz): 27.05, 39.05, 68.50, 136.50, 140.70, 141.95, 142.17, 142.33, 142.81, 143.35, 143.50, 149.80, 145.70, 146.08, 146.31, 146.50, 146.60, 147.80, 156.75. - UV/VIS (5.86x10^{-4} M): 710 (2.38), 636 sh (2.48), 438 (3.41), 408 sh(3.50), 324 sh(4.27). FAB-MS: 805 (20), 804 (33), 803 ((M+1)$^+$, 34), 769 (37), 768 (57), 767 (100), 750(54), 722(76), 721 ((C_{60}+1)$^+$, 73), (high-resolution - MS: 803.0773 (M+H)$^+$, required for $C_{66}H_{11}$: 803.0861).

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