Achiral and Chiral Higher Adducts of C_{70} by *Bingel* Cyclopropanation

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Dedicated to Prof. *Duilio Arigoni* on the occasion of his 70th birthday

Five optically active isomeric C_{70} bis-adducts with (*R*)-configured chiral malonate addends were prepared by *Bingel* cyclopropanation (*Scheme 1*) and their circular dichroism (CD) spectra investigated in comparison to those of the corresponding five bis-adducts with (*S*)-configured addends (*Fig. 2*). Pairs of diastereoisomers, in which the inherently chiral addition patterns on the fullerene surface have an enantiomeric relationship, display mirror-image shaped CD spectra that are nearly identical to those of the corresponding pairs of enantiomers (*Fig. 3*, *b* and *c*). This result demonstrates that the *Cotton* effects arising from the chiral malonate addends are negligible as compared to the chiroptical contribution of the chirally functionalized fullerene chromophore. A series of four stereoisomeric tetrakis-adducts (*Fig. 4*) was prepared by *Bingel* cyclopropanation starting from four stereoisomeric bis-adducts. A comparison of the CD spectra of both series of compounds showed that the magnitude of the *Cotton* effects does not decrease with increasing degree of functionalization (*Fig. 5*). *Bingel* cyclopropanations of C_{70} in Me_2SO are dramatically faster than in apolar solvents such as CCl_4, and the reaction of bis-adducts (±)-**13** and **15** with large excesses of diethyl 2-bromomalonate and DBU generated, *via* the intermediacy of defined tetrakis-adducts (±)-**16** and **17**, respectively, a series of higher adducts including hexakis-, heptakis-, and octakis-adducts (*Table 1*). A high regioselectivity was observed up to the stage of the hexakis-adducts, whereas this selectivity became much reduced at higher stages of addition. The regioselectivity of the nucleophilic cyclopropanations of C_{70} correlates with the coefficients of the LUMO (*l*owest *u*noccupied *m*olecular *o*rbital) and LUMO + 1 at the positions of preferential attack calculated by restricted *Hartree-Fock* – self-consistent field (*RHF-SCF*) methods (*Figs. 9–11*). Based on predictions from molecular-orbital calculations (*Fig. 11*) and the analysis of experimental ^{13}C-NMR data (*Fig. 7, a*), the structure of a unique hexakis-adduct ((±)-**22**, *Fig. 12*), prepared from (±)-**13**, was assigned. The C_2-symmetrical compound contains four 6–6-closed methanofullerene sub-structures in its polar regions (at the bonds C(1)–C(2), C(31)–C(32), C(54)–C(55), and C(59)–C(60)), and two 6–5-open methanofullerene sub-structures parallel to the equator (at C(22)–C(23) and C(26)–C(27)). The 6–5-open sub-structures are formed by malonate additions to near-equatorial 6–5 bonds with enhanced LUMO coefficients, followed by valence isomerization (*Fig. 12*).

1. Introduction. – The covalent chemistry of the higher fullerenes attracts increasing interest since it is becoming clear that reactivity and selectivity of reactions with the larger carbon spheres, C_{70} and beyond, differ significantly from those observed for the more abundant buckminsterfullerene, C_{60} [1]. In particular, the chemical reactivity of C_{70} (*Fig. 1*) has been increasingly investigated [1–3], since it is the most abundant higher fullerene. Although nucleophilic attacks and cycloadditions to C_{70} usually occur at the most curved 6–6 bonds (bonds at the intersect between two six-membered rings) in the polar regions, benzyne was recently shown to add across a closed 6–5 bond; an

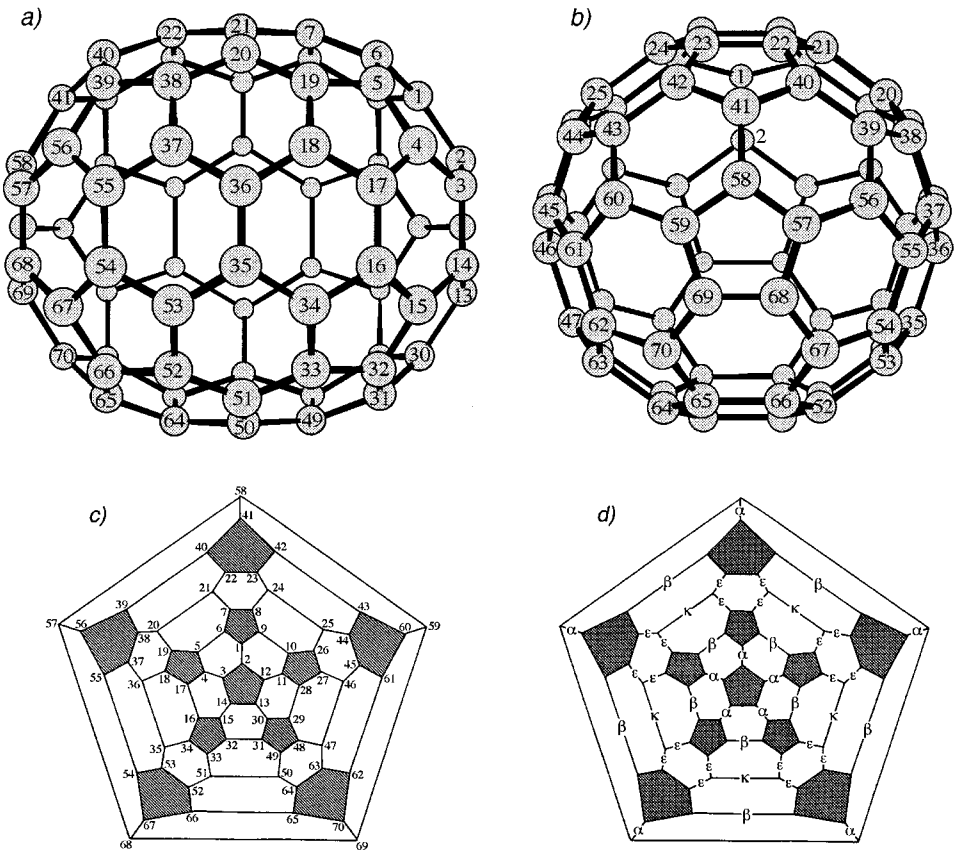

Fig. 1. *Views on* D_{5h}-C_{70} a) *perpendicular to and* b) *along the* C_5-*symmetry axis, and* Schlegel *diagrams showing* c) *the numbering (*clockwise*) of the C-atoms and* d) *the four different types* α, β, ε, *and* κ *of 6–6 bonds*[1]). The curvature and reactivity towards nucleophiles decrease from α- to κ-type bonds.

observation without precedence in the chemistry of C_{60} [2a]. Furthermore, multiple nucleophilic additions to C_{70} occur with a remarkable regioselectivity that substantially exceeds that observed for C_{60} [4][1]).

Of particular interest to us have been the chiroptical properties of C_{70} derivatives with a chiral functionalization pattern. We had previously reported the synthesis and characterization of bis-, tris-, and tetrakis-adducts of C_{70} [4] by *Bingel* cyclopropanation [6]. Mono-addition occurs with high selectivity at the most curved α-type bonds (*Fig. 1, d*) [5] at one pole, and the second cyclopropanation occurs selectively at the α-type bonds at the opposite pole. Using a chiral, C_2-symmetrical addend, generated from bis[(*S*)-1-phenylbutyl] 2-bromomalonate, five optically active C_2-symmetrical isomers were obtained [4]. They consist of two constitutionally isomeric pairs of diastereoisomers with inherently chiral fullerene functionalization patterns and a third

[1]) For the classification of fullerene bond types according to curvature, see [5].

constitutional isomer with an achiral C_{2v}-symmetrical addition pattern. The two compounds in each pair of diastereoisomers showed mirror-image-shaped circular dichroism (CD) spectra, indicating that the chiroptical contributions from the enantiomeric residual fullerene chromophores largely dominate those from the chiral addends. Here, we report the preparation of the corresponding isomeric series of C_{70} bis-adducts formed by addition of the enantiomeric bis[(*R*)-1-phenylbutyl] malonate and provide final proof that the CD spectra of diastereoisomeric bis-adducts with isoconfigurational, inherently chiral fullerene addition patterns are, within the uncertainty of the CD measurement, identical.

Furthermore, we became interested in exploring how the chiroptical properties of fullerene derivatives with chiral addition patterns change, when the conjugated π-chromophore of the fullerene is reduced as a result of increasing degree of functionalization. Therefore, we now report the preparation and chiroptical investigation of tetrakis-cyclopropanated C_{70} derivatives with chiral addition patterns. Also, we provide a first account on the preparation and structural characterization of very highly functionalized C_{70} derivatives including hexakis- to octakis-cyclopropanated derivatives[2]). For some of these derivatives, unusual structures must be considered in order to account for the spectral data.

2. Results and Discussion. – 2.1. *Preparation and Characterization of Optically Active Bis-adducts of C_{70}.* We had previously obtained by *Bingel* addition of bis[(*S*)-1-phenylbutyl] 2-bromomalonate to C_{70} a mono-adduct and five isomeric bis-adducts, namely one pair of C_2-symmetrical diastereoisomers (*S*,*S*,*S*,*S*,^{f}*C*)-**1** and (*S*,*S*,*S*,*S*,^{f}*A*)-**2**, a second pair of C_2-symmetrical diastereoisomers (*S*,*S*,*S*,*S*,^{f}*C*)-**3** and (*S*,*S*,*S*,*S*,^{f}*A*)-**4**, and C_2-symmetrical (*S*,*S*,*S*,*S*)-**5** (*Fig. 2*)[3]) [4]. In the two constitutionally isomeric pairs of diastereoisomers, the chirality of the inherently chiral functionalization pattern adds to that of the addends, whereas, in the third constitutional isomer, the chirality only originates from the stereogenic centers of the addends. Later, it was possible to assign the absolute configurations shown for [CD(+)318]-(*S*,*S*,*S*,*S*,^{f}*C*)-**1** and [CD(−)317]-(*S*,*S*,*S*,*S*,^{f}*A*)-**2** from calculations of the theoretical CD spectra and comparison with the experimental CD data [9][4]). On the basis of the close analogy of both positions and signs of the bands over the entire CD spectra (see below), we also assign with confidence the absolute configurations shown in *Fig. 2* for [CD(+)314]-(*S*,*S*,*S*,*S*,^{f}*C*)-**3** and [CD(−)314]-(*S*,*S*,*S*,*S*,^{f}*A*)-**4**.

To prepare the enantiomers to the five bis-adducts already in hands, C_{70} was reacted with I_2 and bis[(*R*)-1-phenylbutyl] malonate ((*R*,*R*)-**6**) in a modified *Bingel* reaction [11] to give a mixture of mono-adduct (*R*,*R*)-**7** (4%) and the five bis-adducts (54%) depicted on the right side of *Fig. 2* (*Scheme 1*).

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[2]) For higher degrees of addition of C_{70}, see [7].

[3]) For the specification of the absolute configuration of inherently chiral fullerenes and fullerene derivatives with a chiral functionalization pattern by a simple descriptor ^{f}*A* (f = fullerene, *A* = anticlockwise) or ^{f}*C* (*C* = clockwise), see [8]. Determination of the configuration of C_{60} and C_{70} derivatives with a chiral functionalization pattern can be easily achieved *via* the following interactive world wide web page: http://www.diederich.chem.ethz.ch/~mac/chirafull.

[4]) For the definition of enantiomers using CD data, see [10].

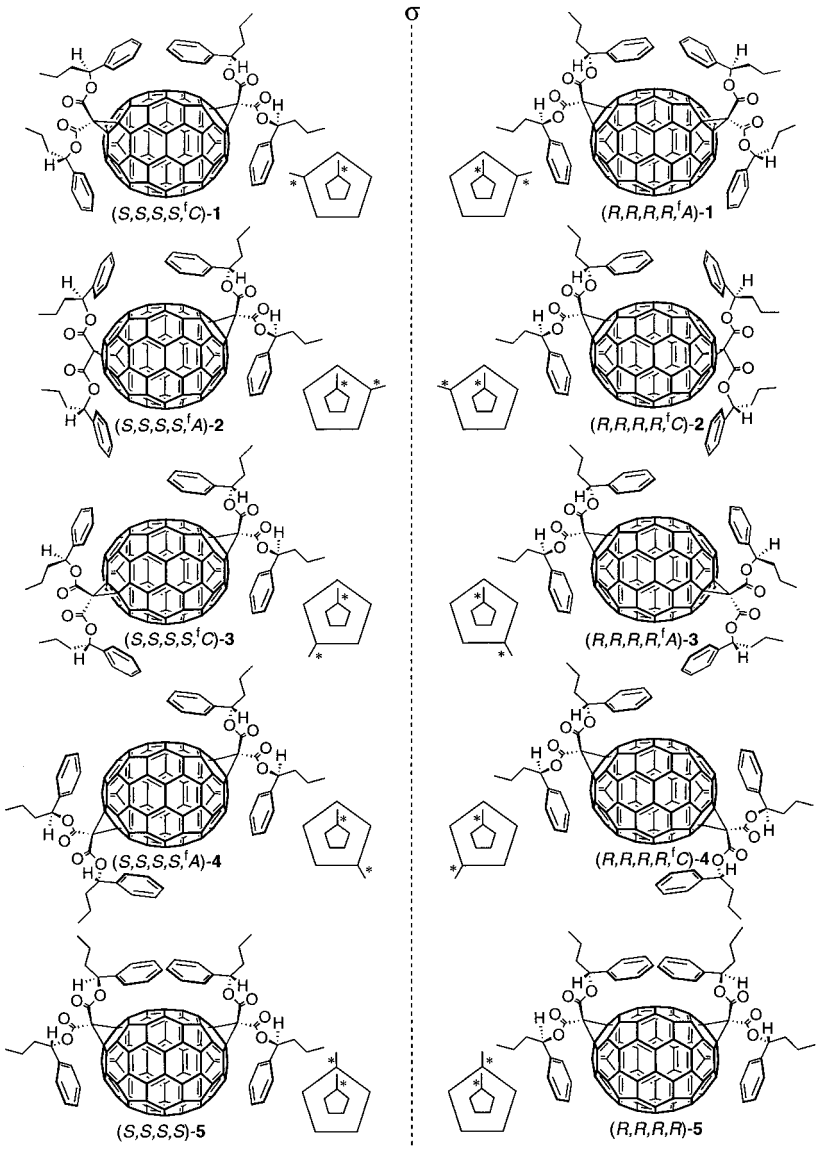
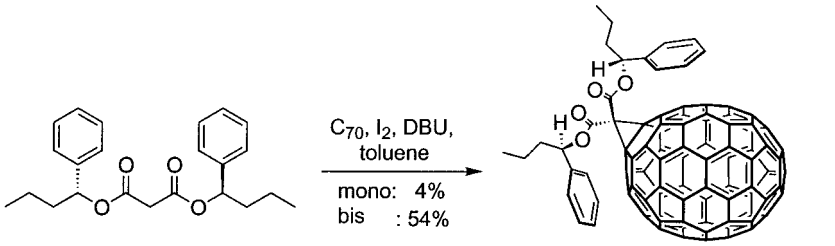


Fig. 2. *All 10 optically active isomeric bis-adducts obtained by* Bingel *addition of bis[(*S*)-1-phenylbutyl] 2-bromomalonate* (left) *and bis[(*R*)-1-phenylbutyl] malonate* (right) *to* C_{70}. Shown are also *Newman*-type projections in which the C_{70} core is viewed along the C_5 axis passing through the proximal (small) and distal (large) pentagon at opposite poles of the fullerene. The vertical line attached to the proximal pentagon depicts the C(1)–C(2) α-type bond where mono-addition occurred. The α-type bonds adjacent to the distal pentagon, which are the sites of second addition, are pointing outside. The star indicates the presence of stereogenic centers with specified absolute configuration in the addends. The arbitrarily chosen position of the star on the right side of the proximal pentagon and on the left side (due to rotation around the C_2 axis) of the distal pentagon refers to the (*S*,*S*)-configuration of the addend. The depiction of the (*R*,*R*)-configuration is the other way around.

Scheme 1. *Synthesis of C_{70} Mono- and Bis-adducts by* Bingel *Addition of (*R,R*)-***6*** to C_{70}*



(*R,R*)-**6**
(1.8 equiv.)

(*R,R*)-**7**
+
5 isomeric bis-adducts
(*R,R,R,R*)-**1** – (*R,R,R,R*)-**5**

The separation of the five isomeric bis-adducts was achieved by preparative HPLC (SiO_2; hexane/PhMe 65:35) yielding five fractions containing (*R,R,R,R,*^{f}*A*)-**1** (*Fraction 4* (elution order)), (*R,R,R,R,*^{f}*C*)-**2** (*Fraction 3*), (*R,R,R,R,*^{f}*A*)-**3** (*Fraction 1*), (*R,R,R,R,*^{f}*C*)-**4** (*Fraction 2*), and (*R,R,R,R*)-**5** (*Fraction 5*). The pure isomers ((*R,R,R,R*)-**1**–(*R,R,R,R*)-**5**) were isolated in a weight ratio of 5.6 : 4.8 : 1.1 : 1 : 2.4, which differs significantly from the ratio (8.8 : 9.3 : 1.4 : 1 : 4.8) obtained in the previously prepared enantiomeric bis-adduct series with (*S*)-configured chiral malonate addends (*Fig. 2*) [4]. Since two different cyclopropanation protocols were applied in the two studies, the product distribution apparently depends on the experimental conditions. Even though diastereoisomeric pairs of bis-adducts were recognizable through the similarity of their ^{13}C-NMR and UV spectra, the assignment of distinct isomers to specific HPLC fractions was not possible in the previous study [4], since absolute configurations had not yet been determined. Based on their enantiomeric relationships, the UV, IR, and ^{1}H- and ^{13}C-NMR spectra of the five new bis-adducts with (*R*)-configured malonate addends are identical to those of the corresponding isomers bearing (*S*)-configured malonate addends.

The CD spectra of the various bis-adducts illustrate in an impressive way the effect of the chiral functionalization pattern of the fullerene core. The spectra of the enantiomers of **5** display only weak *Cotton* effects (*Fig. 3,a*). The $\Delta\varepsilon$ values below 400 nm are assigned to the chiroptical contributions of the chiral malonate addends, whereas the weak effects above 550 nm presumably are best explained by baseline drifts originating from the CD spectrometer[5]).

Much larger *Cotton* effects are recorded for the isomers with chiral functionalization patterns (*Fig. 3,b* and *c*). The spectra show unambiguously, in addition to clear evidence from UV/VIS and ^{1}H- and ^{13}C-NMR spectra, that the pairs **1**/**2** and **3**/**4**, respectively, have the same constitution. Moreover, since the inherently chiral addition patterns on the fullerene surface in each of the four pairs of diastereoisomers

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[5]) We had previously explained these weak *Cotton* effects with an induced CD originating from the perturbation of the achiral fullerene chromophore by the attached chiral addends. While such effects remain possible, studies on two different CD instruments now indicate that the weak bands above 550 nm result predominantly from instrument-dependent baseline drifts.

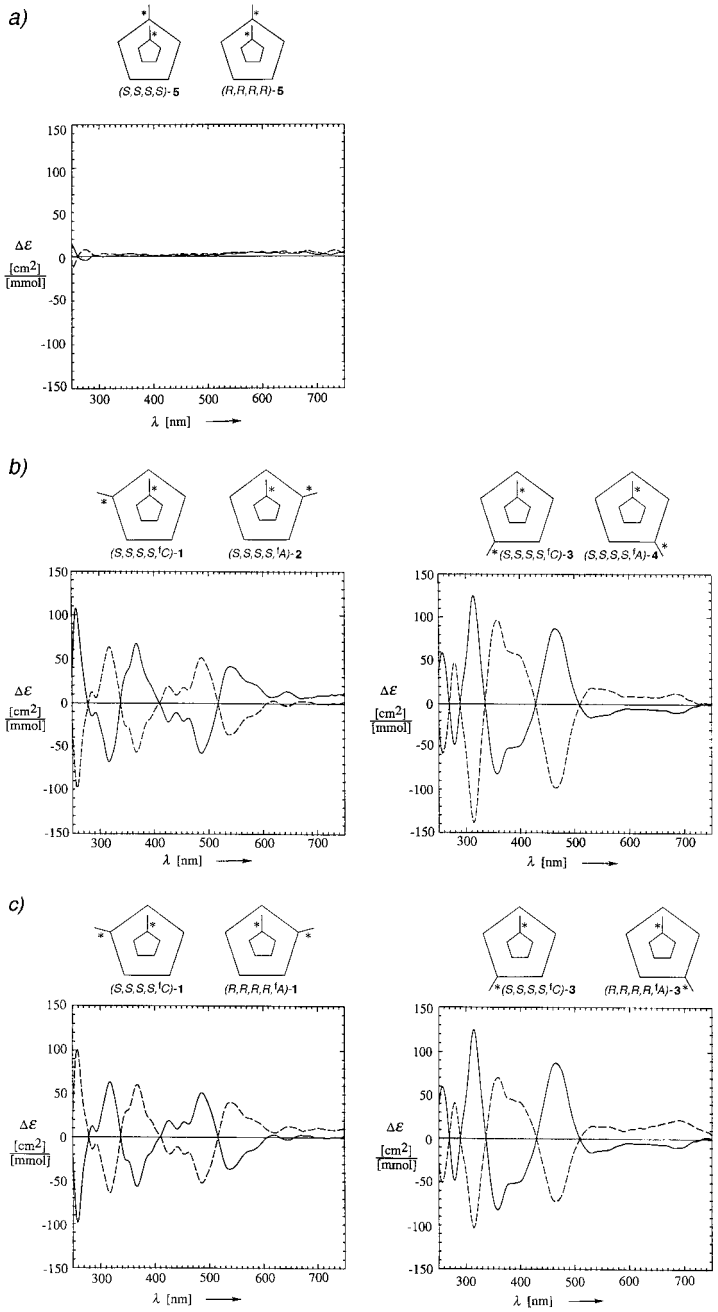


Fig. 3. *CD Spectra in CH_2Cl_2 of* a) *enantiomers (*S,S,S,S*)*-**5** (—)/(R,R,R,R)-**5** (– – –); b) *the pairs of diastereoisomers (*S,S,S,S,^{f}C)-**1** (– – –)/(S,S,S,S,^{f}A)-**2** (—) (left) *and (*S,S,S,S,^{f}C)-**3** (—)/(S,S,S,S,^{f}A)-**4** (– – –) (right); *and* c) *the pairs of enantiomers (*S,S,S,S,^{f}C)-**1** (—)/(R,R,R,R,^{f}A)-**1** (– – –) (left) *and (*S,S,S,S,^{f}C)-**3** (—)/(R,R,R,R,^{f}A)-**3** (– – –) (right)

((*S*,*S*,*S*,*S*,^{f}*C*)-**1**/(*S*,*S*,*S*,*S*,^{f}*A*)-**2**, (*S*,*S*,*S*,*S*,^{f}*C*)-**3**/(*S*,*S*,*S*,*S*,^{f}*A*)-**4**, (*R*,*R*,*R*,*R*,^{f}*A*)-**1**/(*R*,*R*,*R*,*R*,^{f}*C*)-**2**, and (*R*,*R*,*R*,*R*,^{f}*A*)-**3**/(*R*,*R*,*R*,*R*,^{f}*C*)-**4**, resp.) have an enantiomeric relationship, their CD spectra are mirror-image shaped, and, considered pairwise, they are nearly identical to those of the corresponding pairs of enantiomers ((*S*,*S*,*S*,*S*,^{f}*C*)-**1**/(*R*,*R*,*R*,*R*,^{f}*A*)-**1**, (*S*,*S*,*S*,*S*,^{f}*A*)-**2**/(*R*,*R*,*R*,*R*,^{f}*C*)-**2**, (*S*,*S*,*S*,*S*,^{f}*C*)-**3**/(*R*,*R*,*R*,*R*,^{f}*A*)-**3**, and (*S*,*S*,*S*,*S*,^{f}*A*)-**4**/(*R*,*R*,*R*,*R*,^{f}*C*)-**4**, resp.). This clearly demonstrates that the *Cotton* effects resulting from the chiral malonate-ester side chains are negligible as compared to the chiroptical contribution of the chirally functionalized fullerene chromophore.

2.2. *Synthesis and Chiroptical Properties of Optically Pure C_{70} Tetrakis-adducts.* Further cyclopropanation of the stereoisomers (*S*,*S*,*S*,*S*,^{f}*C*)-**1**, (*R*,*R*,*R*,*R*,^{f}*A*)-**1**, (*S*,*S*,*S*,*S*,^{f}*A*)-**2**, and (*R*,*R*,*R*,*R*,^{f}*C*)-**2** was performed to investigate the dependence of the chiroptical contributions of chirally functionalized fullerene chromophores from the degree of addition. For this purpose, the bis-adducts were each reacted with diethyl 2-bromomalonate (11.5 equiv.) and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene; 11.5 equiv.) in CCl_4 for 4.5 d. Column chromatography (SiO_2; CH_2Cl_2/hexane 7:3) yielded the expected tetrakis-adduct stereoisomers (*S*,*S*,*S*,*S*,^{f}*A*)-**8** (from (*S*,*S*,*S*,*S*,^{f}*C*)-**1**), (*R*,*R*,*R*,*R*,^{f}*C*)-**8** (from (*R*,*R*,*R*,*R*,^{f}*A*)-**1**), (*S*,*S*,*S*,*S*,^{f}*C*)-**9** (from (*S*,*S*,*S*,*S*,^{f}*A*)-**2**), and (*R*,*R*,*R*,*R*,^{f}*A*)-**9** (from (*R*,*R*,*R*,*R*,^{f}*C*)-**2**) (*Fig. 4*) in yields varying from 12 to 37%. Note that the configurational descriptor for the chirally functionalized fullerene core changes upon moving from the bis- to the tetrakis-adducts in order to satisfy the rule of the lowest set of locants [8]. The new addends are introduced at bonds with smaller atom numbers (*cf. Fig. 1*) than those at one of the bonds already functionalized in the bis-adducts. Further elution ($CH_2Cl_2 \rightarrow CH_2Cl_2$/MeOH 98 : 2) gave additional fractions containing pentakis-, hexakis-, heptakis-, and octakis-adducts (MALDI-TOF-MS). This was our first experimental evidence for the formation of such higher adducts, and it initiated the investigations described below in *Sect. 2.3.* The formation of tris-adducts [4] was not detected (TLC), probably due to the large excess of bromomalonate used.

The identity of the enantiomeric fullerene functionalization patterns of C_2-symmetrical (*S*,*S*,*S*,*S*,^{f}*A*)-**8** and (*S*,*S*,*S*,*S*,^{f}*C*)-**9** to those of previously reported racemic C_2-symmetrical tetrakis-adducts with achiral malonate addends [4] was established by the similarity of the ^{13}C-NMR and UV/VIS spectra. In addition to the signals observed for the starting bis-adducts, the ^{1}H-NMR spectra of the tetrakis-adducts displayed a *quadruplet* at 4.56 ppm, a *multiplet* around 4.20 ppm, and two *triplets* at 1.50 and 1.20 ppm. These resonances originate from the two newly introduced diethyl-malonate addends. In analogy to the C_2-symmetrical starting bis-adducts, the ^{13}C-NMR spectra of the tetrakis-adducts showed 35 resonances for the fullerene C-atoms, 31 between 160 and 130 ppm, and 4 between 69 and 64 ppm. Four resonances are observed for the C=O groups around 165 ppm, and the signals for the Ph sp^2-C-atoms appear at 139 ppm (two peaks) and between 129 and 126 ppm (six peaks).

The CD spectra (*Fig. 5*) of all four tetrakis-adducts are very similar in shape. Again, no significant differences are observed in the comparison of the spectra assigned to pairs of diastereoisomers having enantiomeric fullerene chromophores with those depicted by pairs of enantiomers. A comparison with the spectra of bis-adducts **1**–**4** (*Fig. 3,b*) shows that the measured *Cotton* effects are of the same order of magnitude and do not decrease with the increasing degree of functionalization. However, the sign of the *Cotton* effects shows some distinct changes upon moving from the bis- to the

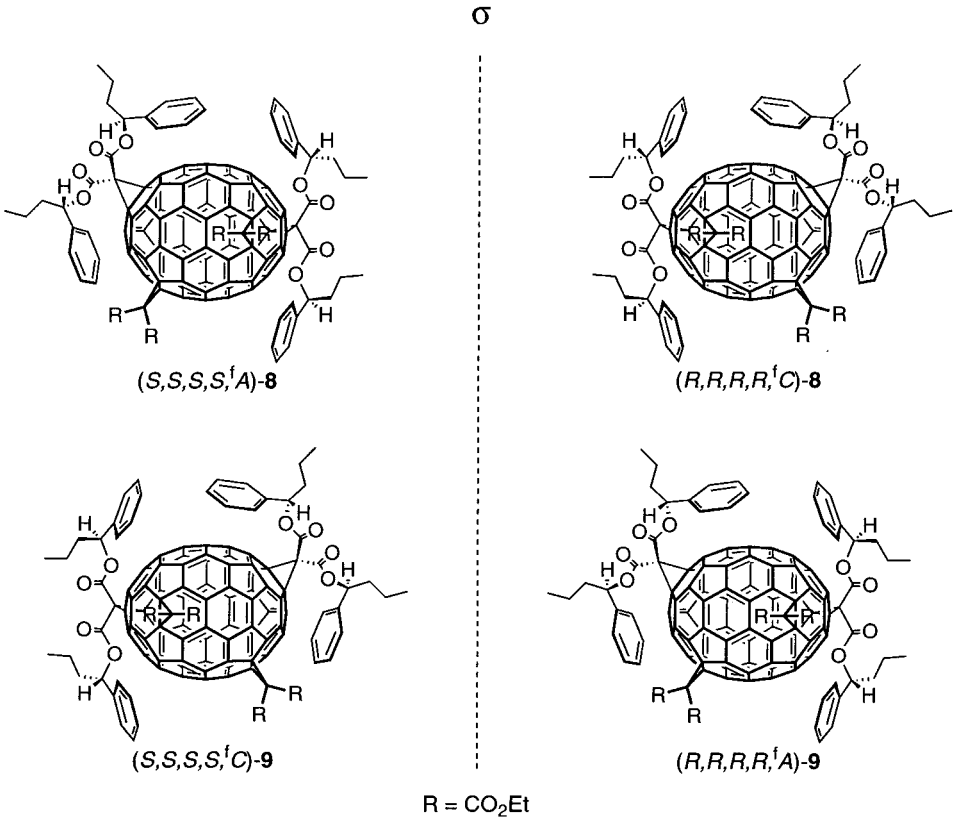


Fig. 4. *Structures of the stereoisomeric tetrakis-adducts of C_{70} prepared by* Bingel *reaction starting from optically pure bis-adducts* **1** *and* **2**

corresponding tetrakis-adducts. Whereas the $\Delta\varepsilon$ values of tetrakis-adduct and starting bis-adduct are similar below $\lambda \approx 400$ nm, there is a sign change observed for the bands appearing above that wavelength. Also, the CD bands in the lower-wavelength region resemble each other more closely than those in the higher-wavelength region. This is shown in *Fig. 6* for tetrakis-adduct (*R*,*R*,*R*,*R*,^{f}*C*)-**8** and the precursor bis-adduct (*R*,*R*,*R*,*R*,^{f}*A*)-**1**. These findings could suggest that the signs of strong CD bands in the higher-wavelength region represent better stereochemical fingerprints, from which the absolute configurations of other related adducts can be derived, than the bands at lower wavelength. The sign of the characteristic strong *Cotton* effect around $\lambda_{max} = 460$ nm, which is found in all CD spectra of bis- and tetrakis-adducts, could serve as such a stereochemical fingerprint.

2.3. *Synthesis of Pentakis- to Octakis-adducts of C_{70}.* 2.3.1. *Solvent-Dependent* Bingel *Cyclopropanations.* The mass-spectrometric evidence for the formation of higher (pentakis- to octakis-) adducts during the preparation of **8**/**9** (*Sect. 2.2*) led us to systematically explore the formation of C_{70} derivatives with a very high degree of addition and try to answer the following questions: How high is the regioselectivity in

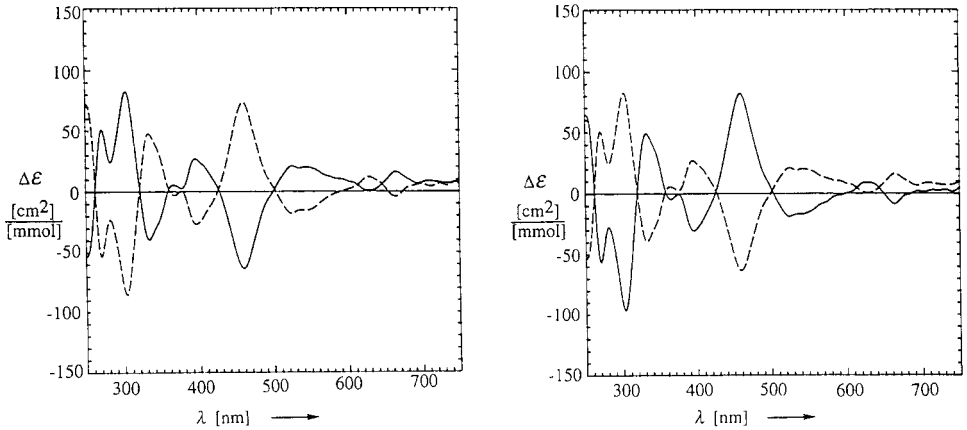


Fig. 5. *CD Spectra in CH_2Cl_2 of the pair of diastereoisomeric tetrakis-adducts (*S,S,S,S,^{f}A*)*-**8** (—) *and (*S,S,S,S,^{f}C*)*-**9** (– – –) (left) *and of the pair of enantiomeric tetrakis-adducts (*S,S,S,S,^{f}A*)*-**8** (– – –) *and (*R,R,R,R,^{f}C*)*-**8** (—) (right)

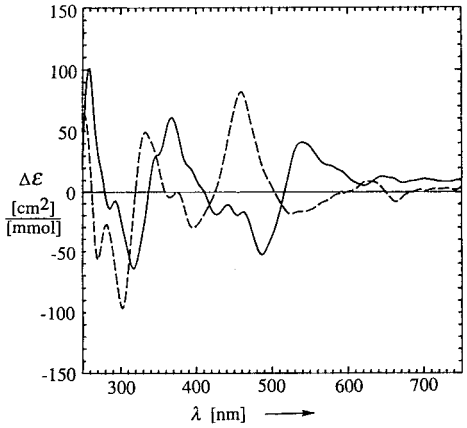
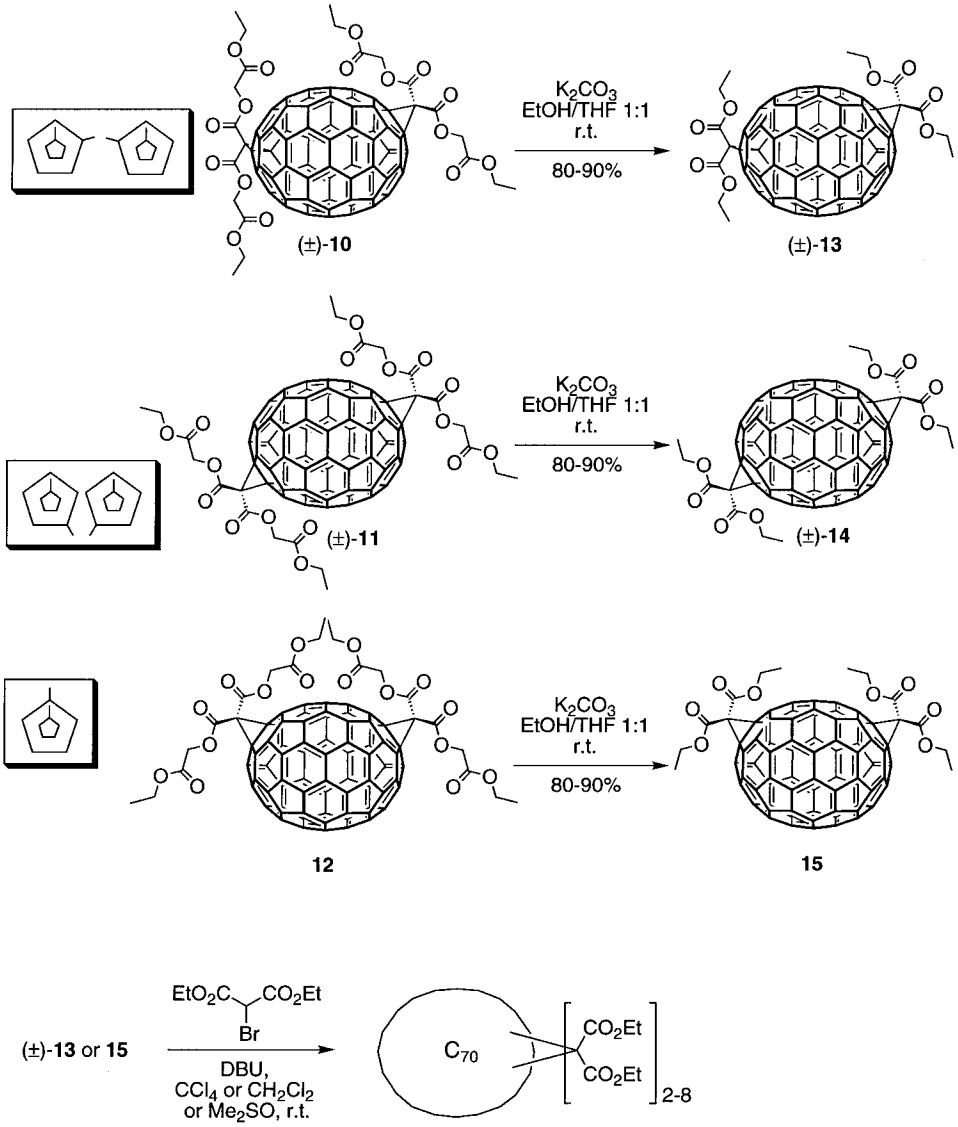


Fig. 6. *CD Spectra in CH_2Cl_2 of tetrakis-adduct (*R,R,R,R,^{f}C*)*-**8** (– – –) *and the precursor bis-adduct (*R,R,R,R,^{f}A*)*-**1** (—)

these higher additions? Are cyclopropanations restricted to the polar regions, or do they occur also in the flatter equatorial region [7] or at 6–5 bonds [2a]? How do the properties of the carbon sphere develop with increasing degree of functionalization?

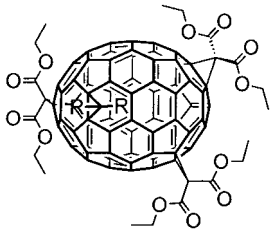
To provide space on the fullerene surface for the strain-free addition of a large number of residues, we decided to perform *Bingel* cyclopropanations with the small diethyl 2-bromomalonate rather than with the bulkier malonate esters used to produce **1**–**5** or bis-adducts (±)-**10**, (±)-**11**, and **12** (*Scheme 2*) [4]. Therefore, we prepared as starting materials for the planned investigations the constitutionally isomeric bis-adducts (±)-**13**, (±)-**14**, and **15**, which had been previously reported by *Bingel* and *Schiffer* [6b], through transesterification (EtOH/THF, K_2CO_3) [12] of (±)-**10**, (±)-**11**, and **12**, respectively (*Scheme 2*).

Scheme 2. *Formation of C_{70} Bis-Adducts* (±)-**13**, (±)-**14**, *and* **15** *by Transesterification, and Conversion of* (±)-**13** *and* **15** *to Higher Adducts*



We first investigated higher adduct formation starting from the racemic bis-adduct (±)-**13**. Conversion with diethyl 2-bromomalonate (8 equiv.) and DBU (8 equiv.) in CCl_4 for 7 d at room temperature, followed by column chromatography (SiO_2; CH_2Cl_2/hexane → CH_2Cl_2) afforded, besides starting material (2%) and a fraction of regioisomeric tris-adducts (32%), only the C_2-symmetrical tetrakis-adduct (±)-**16** (45%), having the same addition pattern as **8**/**9** or a tetrakis-adduct previously

prepared from (±)-**10** [4]. No other regioisomeric tetrakis-adduct was detected which provides further evidence for the high regioselectivity seen in nucleophilic additions to C_{70} leading up to the stage of a tetrakis-adduct [4].



(±)-**16** R = CO_2Et

In *Bingel*-type cyclopropanations of C_{60}, we had previously observed a significant solvent dependency: with increasing solvent polarity, the reactions became accelerated, although at the cost of a reduced selectivity [13]. Thus, multiply functionalized derivatives of C_{60} underwent additional cyclopropanations when the solvent was changed from apolar CCl_4 and PhMe to CH_2Cl_2 or THF, and to Me_2SO [13]. We decided to take advantage of the enhanced reactivity in more polar solvents in order to promote the formation of more highly cyclopropanated derivatives of C_{70}. The reaction of (±)-**13** with diethyl 2-bromomalonate (8 equiv.) and DBU (8 equiv.) in CH_2Cl_2 indeed led to complete conversion of starting material within one day only. Addition of a larger excess of reagents (24 equiv. of bromomalonate and DBU, resp.) and extension of the reaction time to 9 d did not lead to further changes in the product composition (TLC), and chromatographic purification gave tetrakis-adduct (±)-**16** as the only isolable compound. Thus, the reaction in CH_2Cl_2, as compared to the one in CCl_4, was much more rapid, occurred with the same selectivity, but did not yield isolable amounts of multiple adducts beyond the stage of tetrakis-addition.

This situation changed dramatically when the cyclopropanations were conducted in Me_2SO. When a suspension of (±)-**13** in Me_2SO was treated at room temperature with diethyl 2-bromomalonate (8 equiv.) and DBU (8 equiv.), a homogenous solution had formed within 2 h, and TLC indicated complete conversion of the starting material. Chromatographic workup (SiO_2; $CH_2Cl_2 \rightarrow CH_2Cl_2$/AcOEt 5:1; then SiO_2-*H*, $CH_2Cl_2 \rightarrow CH_2Cl_2$/AcOEt 95:5) yielded six product fractions which were identified by FAB-MS as containing pentakis-, hexakis-, and heptakis-adducts in addition to tetrakis-adduct (±)-**16** (*Table*, *Entry A*). The isolation of (±)-**16** could suggest that this tetrakis-adduct is an intermediate in the formation of all of the isolated higher adducts, although it cannot be excluded that other tetrakis-adducts are also formed as intermediates which are more reactive and, therefore, cannot be detected. The main product in *Entry A* (*Table*) is a C_2-symmetrical hexakis-adduct (^{13}C-NMR, *Fig. 7,a*), and a proposal for its structure will be made in *Sect. 2.3.2* below.

In a second run, all starting bis-adduct (±)-**13** was completely dissolved when the reagents were added, and ten product fractions were isolated (*Entry B* in the *Table*) and identified by FAB-MS as hexakis- to octakis-adducts. *Fraction I* is a C_1-symmetrical heptakis-adduct, depicting, in the ^{13}C-NMR spectrum ($CDCl_3$, 125.8 MHz), 54 of the 56 expected fullerene sp^2-C-atom resonances, two of which display double intensity.

Table. *Higher Adducts of* C_{70} *formed by* Bingel *Cyclopropanation of Bis-adducts* (±)-**13** *and* **15** *with Diethyl 2-Bromomalonate*[a]) *and DBU*[a]) *in* Me_2SO *at Room Temperature*

Entry	Starting Material	Product *Fraction*[b])	Nature of Product (Yield [%])[c])
A[d])	(±)-**13**	*I*	Tetrakis-adduct (±)-**16** (6)
		II	Pentakis-adduct(s) (7)
		III	Hexakis-adduct(s) (9)
		IV	C_2-Hexakis-adduct (±)-**22** (21)[e])
		V	Heptakis-adduct(s) (12)
		VI	Heptakis-adduct(s) (3)
B[f])	(±)-**13**	*I*	C_1-Heptakis-adduct (5)[e])
		II	C_2-Hexakis-adduct[e,g]) and C_1-Heptakis-adduct (5)[e])
		III	C_1-Heptakis-adducts (24)[e])
		IV	Heptakis-adduct(s) (2)
		V	Octakis-adduct(s) (3)
		VI	C_2-Octakis-adduct (6)[e])
		VII	C_1-Octakis-adduct (7)[e])
		VIII	Octakis-adduct(s) (3)
		IX	Octakis-adduct(s) (3)
		X	C_1-Octakis-adduct (3)[e])
C[d])	**15**	*I*	Bis-adduct **15** (4)
		II	Tetrakis-adduct **17** (8)
		III	Pentakis-adduct(s) (3)
		IV	Hexakis-adduct(s) (5)
		V	C_2-Octakis-adduct (13)[e])
		VI	Octakis-adduct(s) (6)
		VII	Octakis-adduct(s) (1)

[a]) Amount of the two reagents: 8 equiv. in the conversions of (±)-**13** and 6 equiv. in the conversion of **15**. [b]) Listed according to the chromatographic sequence of elution; degree of addition determined by FAB-MS. [c]) Yields of isolated material. [d]) Reaction time: 2 h. [e]) Symmetry of the product according to the ^{13}C-NMR spectrum. [f]) Reaction time: 2.5 h. [g]) Identical to hexakis-adduct of *Entry A*, *Fraction IV*.

Fraction II contained the C_2-symmetrical hexakis-adduct, which was the main product in the previous run, in addition to presumably a C_1-symmetrical heptakis-adduct. *Fraction III* contained a mixture of two C_1-symmetrical heptakis-adducts. The ^{13}C-NMR spectrum of *Fraction VI* (*Fig. 7,b*) depicted 8 resonances for C=O groups, 27 signals for fullerene sp^2-C-atoms, 19 signals for fullerene sp^3-C-atoms, CH_2 groups, and the bridging methano C-atoms, as well as 8 resonances for Me groups. These spectroscopic data are compatible with the presence of a C_2-symmetrical octakis-adduct of C_{70}. *Fractions VII* and *X* finally contain each one C_1-symmetrical octakis-adduct, as evidenced by the presence of 54 (*Fraction VII*) and 51 (*Fraction X*) out of the 54 expected fullerene sp^2-C-atom resonances. All other fractions were not investigated by ^{13}C-NMR due to the small amounts of material available.

These experiments clearly demonstrate the higher reactivity of the *Bingel* addition in the dipolar-aprotic solvent Me_2SO as compared with the less polar solvent CH_2Cl_2 and apolar CCl_4. They also provide good evidence that the regioselectivity in all three

solvents is unchanged up to the stage of tetrakis-adduct (±)-**16**, which is isolated as the only tetrakis-adduct in all runs. Furthermore, the high regioselectivity observed in this study and previous work [4] for the formation of mono- to tetrakis-adducts seems to

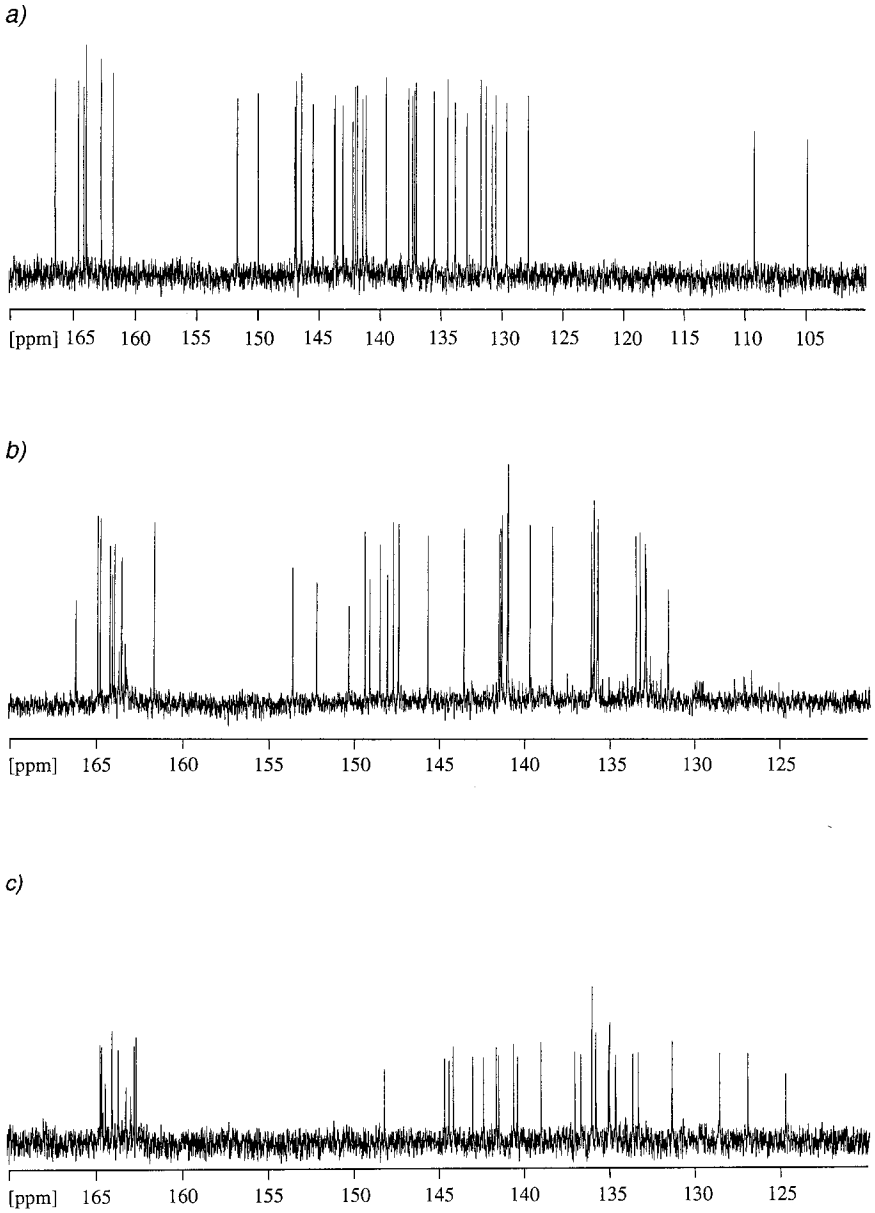
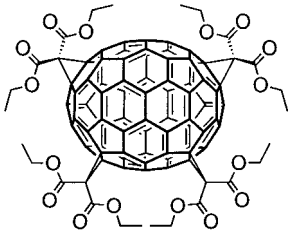


Fig. 7. *Fullerene sp^2-C-atom resonances in the ^{13}C-NMR spectra* (125.8 MHz, $CDCl_3$, *ca.* 40 mM [$Cr(acac)_3$]) *of* a) *the* C_2*-symmetrical hexakis-adduct* (±)-**22** *of* Entry A, Fraction IV (Table), b) *the* C_2*-symmetrical octakis-adduct of* Entry B, Fraction VI (*Table*), and c) *the* C_2*-symmetrical octakis-adduct of* Entry C, Fraction V (*Table*)

extend to the stage of the hexakis-adduct, since only two such adducts were isolated (*Table*, *Entries A* and *B*). However, this selectivity is lost upon moving to heptakis- and octakis-adducts, yielding a variety of regioisomers which could not be identified structurally.

The formation of higher adducts was also investigated starting from the C_{2v}-symmetrical bis-adduct **15**. The *Bingel* reaction (6 equiv. of diethyl 2-bromomalonate and DBU, resp.) in Me_2SO yielded, after stirring for 2 h at room temperature and chromatographic workup (SiO_2; $CH_2Cl_2 \rightarrow CH_2Cl_2$/AcOEt 5:1; then SiO_2-*H*; $CH_2Cl_2 \rightarrow CH_2Cl_2$/AcOEt 95:5), a small amount of starting material besides 6 other product fractions (*Entry C* in the *Table*). Among the most abundant compounds formed was the tetrakis-adduct **17**, with identical addition pattern to that previously obtained in the cyclopropanation of **12** with an excess of diethyl 2-bromomalonate in CCl_4 [4]. The C_{2v}-symmetry of **17** was clearly revealed by the ^{13}C-NMR spectrum which displayed 3 signals for the C=O, CH_2, and Me groups, respectively, of the diethyl malonates, 18 resonances for fullerene sp^2-C-atoms, 3 resonances for fullerene sp^3-C-atoms, and 2 peaks for the methano-bridge C-atoms.



17

The main product of the cyclopropanation of **15** was a C_2-symmetrical octakis-adduct (*Fraction V*, *Entry C* in the *Table*). The symmetry assignment was supported by the ^{13}C-NMR spectrum (*Fig. 7,c*), which depicted 8 signals for C=O groups, 25 resonances (two with double intensity) for fullerene sp^2-C-atoms, 19 peaks between 33 and 75 ppm for the fullerene sp^3-C-atoms, CH_2 groups, and methano-bridge C-atoms, and five signals for Me groups. Based on these data, a structural proposal is not possible. The multiple cyclopropanation of **15** resembles in its outcome that of (±)-**13**: one tetrakis-adduct apparently forms exclusively, and a considerable regioselectivity is retained up to the stage of the hexakis-adducts but lost subsequently in the conversion to even more highly functionalized derivatives. Interestingly, the constitutionally isomeric C_2-symmetrical octakis-adducts (obtained from the two precursors (±)-**13** and **15**) display strongly different electronic absorption spectra (*Fig. 8*). The end absorption (the optical HOMO-LUMO gap; HOMO = *h*ighest *o*ccupied *m*olecular *o*rbital; LUMO = *l*owest *u*noccupied *m*olecular *o*rbital) of the green-colored octakis-adduct obtained from **15** (*Fraction V*, *Entry C* in the *Table*) appears at *ca.* 720 nm (1.72 eV), which is in the range of the end absorptions measured for the lower adducts of C_{70}. In contrast, the end absorption of brown-red colored octakis-adduct produced from (±)-**13** (*Fraction VI*, *Entry B* in the *Table*) is strongly hypsochromically shifted and appears at *ca.* 530 nm (2.34 eV). This high-energy optical gap suggests that the

conjugated π-electron chromophore of the fullerene has been substantially disrupted by the addition of the functional groups, presumably under formation of more localized benzenoid sub-structures. A similar reduction in the conjugated π-chromophore has been observed in pseudo-octahedral hexakis-adducts of C_{60} which, as a result, are yellow and also display a strongly hypsochromically shifted end absorption [13a] [14] [15a].

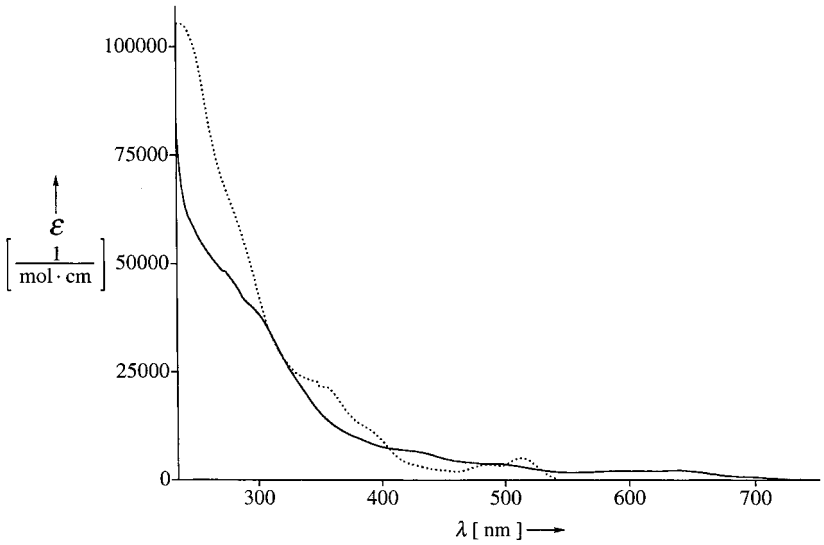
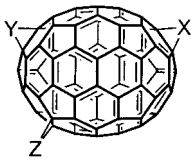


Fig. 8. *UV/VIS Spectra in CH_2Cl_2 of the C_2-symmetrical octakis-adducts formed by cyclopropanation of* (±)-**13** (*Fraction VI, Entry B* in the *Table*) (·····) and **15** (*Fraction V, Entry C,* in the *Table*) (—)

2.3.2. *Theoretical Investigations on the Regioselectivity of Nucleophilic Cyclopropanations of C_{70} and Structure Proposed for a C_2-symmetrical Hexakis-adduct of C_{70}.* *Hirsch* and co-workers [15] had shown by semi-empirical AM1 calculations [16] that the regioselectivity of multiple nucleophilic cyclopropanations of C_{60} correlated with the coefficients of the frontier orbitals (LUMO and LUMO + 1) at the positions of preferential attack. We constructed the molecular geometries of the C_{70} adducts **18** – **20**, in which the malonate addends are substituted by CH_2 bridges to save computing time, with the help of the program CHEMCAM [17]. Subsequently, geometries were optimized at the semi-empirical MNDO level [18] using the MNDO94 Program [19]. Starting from the MNDO-optimized geometries, single-point *ab initio* RHF-SCF (restricted *Hartree-Fock*, self-consistent field) calculations with the 3-21G basis set were carried out using GAUSSIAN 94 [20]. In spite of the relatively small basis set, the results give a reasonable qualitative description of the molecular systems. Test calculations on the C_s-symmetrical mono-adduct **18** with the 6-31G* basis set did not fundamentally change the shape of the first nearly isoenergetic LUMOs obtained with the 3-21 G basis set.

Experimentally, cyclopropanation of mono-malonate adduct $C_{71}(COOEt)_2$ is found to occur at the α-type bonds at the pole opposite to the already functionalized one to give (±)-**13** as the major bis-adduct, followed by **15**, and (±)-**14** as the minor product [4]



18 X = CH_2; Y = —; Z = —
19 X = CH_2; Y = CH_2; Z = —
20 X = CH_2; Y = CH_2; Z = CH_2

(see also *Sect. 2.1*). Calculations of mono-adduct **18** were in agreement with these experimental results and showed that the LUMO coefficients are particularly high at the α-type C(56)–C(57) and C(59)–C(60) bonds at the nonfunctionalized pole, which are cyclopropanated to yield the major product (±)-**13** (*Fig. 9*). The formation of achiral **15** is explained by the enhanced coefficients, at the C(41)–C(58) bond, of the LUMO + 1, which is nearly isoenergetic ($\Delta E = 0.07$ kcal mol^{-1}) with the LUMO. The bonds C(67)–C(68) and C(69)–C(70) only display small coefficients of both LUMO and LUMO + 1, which accounts for the formation of (±)-**14** as the minor product only.

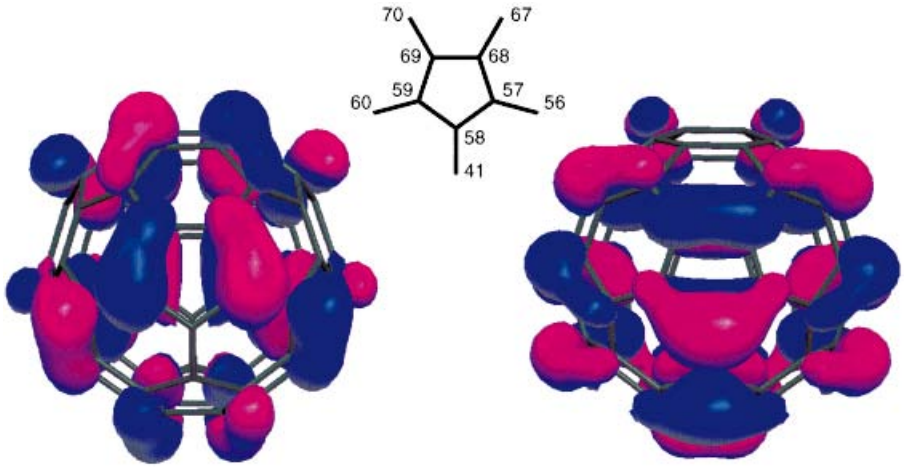


Fig. 9. *Calculated* (RHF-SCF/6-31G*) *LUMO* (left) *and LUMO + 1* (right) *of mono-adduct* **18**. (Visualization of the molecular orbitals was achieved with MOLEKEL 2.5 [21]). Shown is the unfunctionalized pole opposite to the one at which the mono-addition had occurred at the C(1)–C(2) bond. Also shown is the numbering of the bonds at which the second addition occurs.

The calculations also reproduced well the observed preferential formation of a single, C_s-symmetrical tris-adduct (not shown; addition pattern as in **20** [4]) and a single C_{2v}-symmetrical tetrakis-adduct **17** starting from bis-adduct **15**. The calculated bis-adduct **19** (resembling **15**) depicted enhanced LUMO coefficients at the β-type bonds C(31)–C(32) and C(65)–C(66) either of which gives the isolated tris-adduct upon mono-cyclopropanation (*Fig. 10*). Similarly, tris-adduct **20** displays in the LUMO + 1 (ΔE(LUMO + 1 – LUMO) = 0.3 kcal mol^{-1}) enhanced coefficients at the β-type bond which, in the corresponding tris-malonate-adduct, is cyclopropanated to yield **17**.

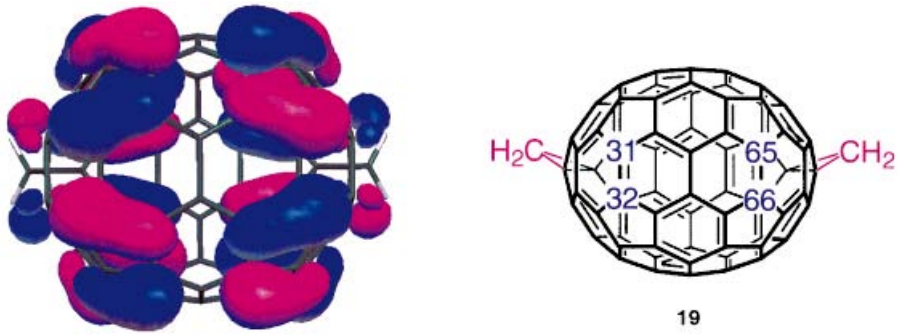


Fig. 10. *Calculated* (RHF-SCF/3-21G) *LUMO of the* C_{2v}*-symmetrical bis-adduct* **19**. Also shown are the bonds C(31)–C(32) and C(65)–C(66) that show the highest LUMO coefficients and are attacked in the regioselective formation of a C_s-symmetrical tris-adduct with a functionalization pattern as in **20**.

Having demonstrated that frontier-molecular-orbital calculations nicely reproduce the experimental product distribution in the nucleophilic cyclopropanation of C_{70} up to the formation of tetrakis-adducts, we felt comfortable to apply such analysis, together with the evaluation of ^{13}C-NMR spectroscopic data, to make a structural proposal for the C_2-symmetrical hexakis-adduct isolated in the higher cyclopropanation of bis-adduct (±)-**13** (*Fraction IV*, *Entry A* in the *Table*). This proposal includes the following assumptions: *i*) The formation of the hexakis-adduct proceeds *via* tetrakis-adduct (±)-**16** as intermediate. This is a reasonable assumption, since no evidence for the formation of any other tetrakis-adduct was obtained (*Sect. 2.3.1*). *ii*) No cyclopropanations occur at the biphenyl type 6–6 bonds along the equator of the fullerene. *iii*) For steric reasons, additions do not occur at 6–6 bonds located in hexagons which already bear a functional group [15c]. *iv*) In view of the findings by *Meier et al.* [2a], who reported formation of a 6–5 closed adduct ('closed' bond at the junction between a hexagon and a pentagon) by [2+2] cycloaddition of benzyne to the C(7)–C(8) bond of C_{70}, cyclopropanations at this and the other corresponding 6–5 bonds, although not previously reported, should also be taken into consideration.

The ^{13}C-NMR spectrum (*Fig. 7,a*) of the hexakis-adduct (*Fraction IV*, *Entry A* in the *Table*) displayed 6 resonances for C=O and CH_2 groups, respectively, 5 peaks for Me groups, 31 signals for fullerene sp^2-C-atoms, 4 lines for fullerene sp^3-C-atoms, and 3 signals for methano-bridge C-atoms. The number of observed peaks is in agreement with a C_2-symmetrical hexakis-adduct, but the positions of the resonances do not match those expected for the fusion of six cyclopropane rings to the C_{70} core: two fullerene sp^2-C-atom signals are in excess and two fullerene sp^3-C-atom signals are missing. Furthermore, two fullerene sp^2-C-atom resonances display a remarkable upfield shift to 109.34 and 105.01 ppm, respectively, and the resonance of one of the methano-bridge C-atoms appears unusually downfield-shifted (above 63 ppm).

Subsequent MO calculations on (±)-**21** (*Fig. 11*) (as a model for (±)-**16**) showed that bonds with high LUMO coefficients that meet the above-made assumptions are the 6–5 bonds C(7)–C(8), C(22)–C(23), C(26)–C(27), and C(44)–C(45). Enhanced LUMO+1 coefficients were also observed for the sterically accessible 6–6 bonds C(21)–C(22) and C(27)–C(46).

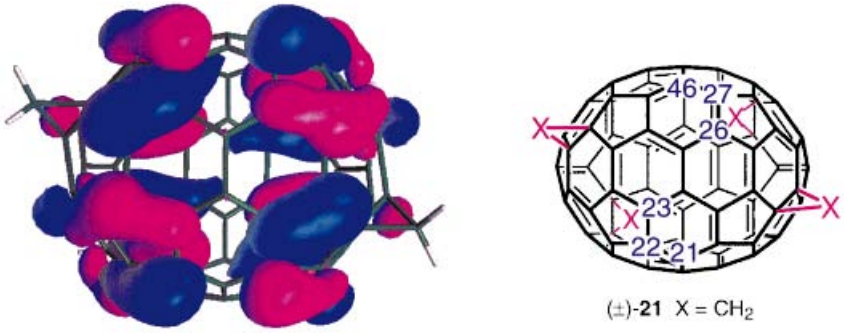


Fig. 11. *Calculated* (RHF-SCF/3-21G) *LUMO of tetrakis-adduct (±)-***21**. Also shown are the 6–5 bonds C(22)–C(23) and C(26)–C(27) that are sterically accessible to cyclopropanation and display high LUMO coefficients. The bonds C(21)–C(22) and C(27)–C(46) reveal high LUMO + 1 coefficients (not shown).

Taking into account the computational and experimental results as well as the findings by *Meier et al.* [2a], we propose the unique structure (±)-**22** (*Fig. 12*) for the C_2-symmetrical hexakis-adduct. Attack at tetrakis-adduct (±)-**16** occurs at the 6–5 bonds C(22)–C(23) and C(26)–C(27)[6]), characterized by enhanced LUMO coefficients, under formation of an intermediate hexakis-cyclopropanated derivative (±)-**23**. However, since 6–5-open methanofullerenes are calculated to be much more stable than 6–5-closed derivatives [22], rapid valence isomerization occurs under formation of (±)-**22**, with two 6–5 open methanofullerene sub-structures.

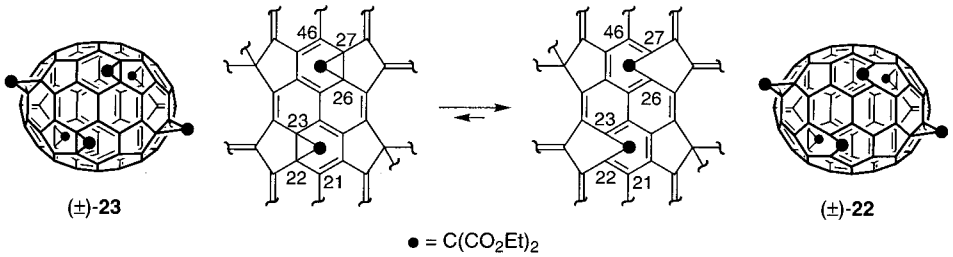


Fig. 12. *Valence isomerization of the* C_2*-symmetrical hexakis-adduct (±)-***23** *with two 6–5-closed bonds, initially formed in the cyclopropanation of (±)-***16**, *into the more stable* C_2*-symmetrical structure (±)-***22**, *containing two 6–5-open 'bonds'*

The ^{13}C-NMR data can now be rationalized. The two upfield shifted fullerene sp^2-C-atom resonances are those of the bridgehead C-atoms in the two 6–5-open methanoannulene sub-structures and the downfield resonance of one methano bridge C-atom (above 63 ppm) belongs to the bridging C-atom in these sub-structures. These

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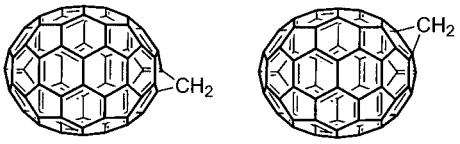
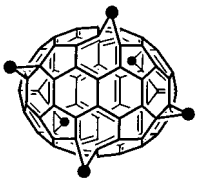
[6]) For reasons of clarity and ease of comparison, the numbering scheme of the tetrakis-adduct is maintained here. Note however that in (±)-**22**, the 6–5-open bridges, constituting structural 'homo' modifications of the fullerene core, formally have to be assigned the lowest possible locants, namely 7,8 and 37,38. The 6–6-closed methano bridges then are located at positions 3,4 : 28,29 : 41,58 : 65,66. In the hexakis-adduct (±)-**23**, on the other hand, the overall lowest set of locants for the six methano addends is 1,2 : 18,19 : 22,23 : 31,32 : 56,57 : 61,62.

assignments are further supported by the ^{13}C-NMR data for the 6–5-open methano[70]fullerene **24** reported by *Smith* and co-workers [23]. The resonance for the bridgehead C-atoms in this 6–5-open derivative appears at 118.74 ppm, and the signal for the bridging methano C-atom is observed at 34.00 ppm. As a comparison, the corresponding resonances in the 6–6-closed isomer **25** appear at 64.06 and 62.56 (bridgehead C-atoms) and 13.80 ppm (methano-bridge C-atom). Upon changing from a 6–6-closed to a 6–5-open methanofullerene structure, bridgehead and methano-bridge C-atom resonances move downfield.



24 **25**

A second structure is, in principle, in agreement with the computational and experimental data. Cyclopropanation at the 6–6 bonds C(21)–C(22) and C(27)–C(46) (*Fig. 11*) with enhanced LUMO + 1 coefficients could lead to a hexakis-cyclopropanated C_{70} derivative which, upon 6–6-closed to 6–6-open valence isomerization, would generate a C_2-symmetrical hexakis-adduct (*Fig. 13*), whose ^{13}C-NMR data could match those observed experimentally. We dismiss this structural alternative for the hexakis-adduct, since 6–6-open methanofullerenes are calculated to be energetically much less favorable than 6–5-open ones [22]. However, the intermediate formation of a non-valence-isomerized hexakis-cyclopropanated adduct, resulting from addition to the C(21)–C(22) and C(27)–C(46) bonds, on the way to the octakis-adducts isolated in *Entry B* (*Table*) cannot be excluded. All three octakis-adducts (*Fractions VI*, *VII*, and *X*), which were analyzed by ^{13}C-NMR spectroscopy, are lacking the resonances around 110 ppm that are highly characteristic of 6–5-open methanofullerene sub-structures. This suggests that (±)-**22** is not an intermediate in their formation, and that they are presumably formed *via* the intermediacy of a hexakis-adduct with six fused cyclopropane rings.



● = $C(CO_2Et)_2$

Fig. 13. *Depiction of a less probable structure for the C_2-symmetrical hexakis-adduct obtained by cyclopropanation of (±)-***16**

From an electronic viewpoint, the proposed structure (±)-**22** features several advantages. In the assigned addition pattern, no extra double bonds are located in pentagons, and the compound displays a total of five (energetically unfavorable [24])

intrapentagonal double bonds, just like the parent C_{70} [7a] [25]. By the valence isomerization, a part of the π-electron delocalization energy, which is lost upon addition to the bonds C(22)–C(23) and C(26)–C(27) that are part of the equatorial belt of benzenoid rings, is regained. Introducing 6–5-open methanofullerene sub-structures into a fullerene actually represents the least perturbation of its conjugated π-electron chromophore which is not reduced by the structural change [23] [26]. Correspondingly, the UV/VIS spectra of (±)-**22** and its likely precursor, tetrakis-adduct (±)-**16**, are quite similar, both in terms of the shape of the absorption bands and the position of the end absorption (*Fig. 14*).

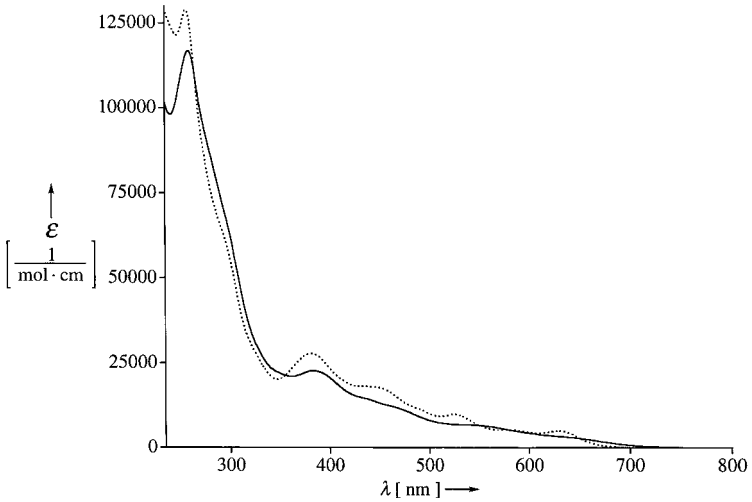


Fig. 14. *Comparison of the UV/VIS spectra in CH_2Cl_2 of hexakis-adduct (±)-***22** (—) *and its likely precursor, tetrakis-adduct (±)-***16** (·····)

3. Conclusions. – This paper makes several important contributions to the understanding of chemical reactivity and physical properties of covalent adducts of C_{70}. The compounds investigated were all prepared by the nucleophilic *Bingel* cyclopropanation reaction which was found to be highly solvent-dependent: upon changing from apolar solvents such as CCl_4 to dipolar aprotic Me_2SO, the rates of addition increase dramatically. First, it was demonstrated, for a series of optically active bis-adducts with inherently chiral addition patterns on the fullerene surface and bearing chiral malonate addends, that the *Cotton* effects resulting from the chiral addends are negligible as compared to the chiroptical contribution of the chirally functionalized fullerene chromophore. The CD spectra of pairs of diastereoisomers, in which the inherently chiral addition patterns have an enantiomeric relationship, are mirror-image-shaped and are nearly identical to those of the corresponding pairs of enantiomers. Secondly, comparisons between the chiroptical properties of optically active bis-adducts and tetrakis-adducts, both with inherently chiral addition pattern, showed that the magnitude of *Cotton* effects does not seem to decrease substantially with an increasing degree of functionalization. Finally, in a third investigation, hexakis- to octakis-adducts of C_{70} were prepared starting from constitutionally isomeric bis-

adducts *via* the intermediacy of unique tetrakis-adducts. A high regioselectivity was observed up to the stage of the hexakis-adducts, whereas this selectivity becomes much reduced at higher stages of addition. Theoretical investigations showed that the regioselectivity of the nucleophilic cyclopropanations of C_{70} correlated with the coefficients of the frontier orbitals (LUMO and LUMO + 1) at the positions of preferential attack. Similarly useful correlations had previously been reported by *Hirsch* and co-workers for the regioselectivity of multiple cyclopropanations of C_{60} [15]. By combining theoretical predictions based on *ab initio* calculations with the analysis of experimental ^{13}C-NMR data, the structure of a unique hexakis-adduct ((±)-**22**) could be confidently elucidated. This C_2-symmetrical compound contains four 6–6-closed methanofullerene sub-structures in its polar regions (at the bonds C(1)–C(2), C(31)–C(32), C(54)–C(55), and C(59)–C(60)), and two 6–5-open methanofullerene sub-structures parallel to the equator (at C(22)–C(23) and C(26)–C(27)). The 6–5-open sub-structures are formed by malonate additions to equator-near 6–5-bonds with enhanced LUMO coefficients, followed by valence isomerization. Such reactivity is unknown in the chemistry of C_{60} and, therefore, this study again clearly demonstrates that a full understanding and appreciation of fullerene reactivity requires the investigation of the covalent chemistry of fullerenes beyond C_{60}.

Experimental Part

1. *General*. Reagents used were reagent-grade commercials. HPLC Solvents were from *Biosolve* and *Fluka*. C_{70} used for the functionalizations was from *Hoechst AG*, Frankfurt am Main, Germany. CH_2Cl_2 and PhMe used for the reactions were dried over molecular sieves (4 Å), THF was distilled from Na/benzophenone, EtOH (abs., ≥99.8% from *Fluka*) from Na/diethyl phthalate, and $(CH_3)_2SO$ from Na immediately before use. TLC: *Polygram SIL G/UV$_{254}$* from *Macherey-Nagel*. Column chromatography (CC): SiO_2 (0.05–0.10 mm, 140–270 mesh) from *Macherey-Nagel* and *Silica Gel H* from *Fluka*. HPLC Columns: *Macherey-Nagel Nucleosil 100-7* SiO_2 (7 μm), 250 mm × 4 mm I.D. and (7 μm) 250 mm × 21 mm I.D. HPLC Instrumentation: *Knauer HPLC Pump 64* high-pressure gradient pumps with anal. or prep. pump heads and vacuum on-line degasser, electrical injection valve, and *Variable Wavelength Monitor* UV/VIS detector from *Knauer*; all chromatograms have been taken at ambient temp. with the detector wavelength fixed at $\lambda = 310$ nm. M.p.: all fullerene derivatives decompose above 250°. UV/VIS Spectra: *Varian-CARY-5* spectrometer; ε [l mol^{-1} cm^{-1}]. CD Spectra: *Jasco J-710* spectropolarimeter; $\Delta\varepsilon$ [cm^2 mmol^{-1}]. ^{1}H- and ^{13}C-NMR Spectra: *Bruker-AMX-500* and *Varian-GEMINI-200* and *-300* spectrometers; δ [ppm] with the solvent peak as reference. MS: MALDI-TOF spectra with reflectron detection were measured in the positive- or negative-ion mode, acceleration voltage 15 kV, on a *Bruker REFLEX* spectrometer; 2,5-dihydroxybenzoic acid (DHB) (0.1M in MeCN/EtOH/H_2O 50:45:5), anthracene-1,8,9-triol (dithranol) (0.05M in $CHCl_3$/MeOH 1:1), or 2,4,6-trihydroxyacetophenone (THA) (0.5M in EtOH)/diammonium citrate (0.1M in H_2O) were used as matrix; FAB spectra were measured on a *VG-ZAB2-SEQ* spectrometer with 2-nitrobenzyl alcohol (NOBA) as matrix.

*Bis[(*R*)-1-phenylbutyl] Malonate* (**6**). As previously described for bis[(*S*)-1-phenylbutyl] malonate [4] with pyridine (1.08 ml, 13.4 mmol), (*R*)-1-phenylbutanol (2.0 g, 13.4 mmol), CH_2Cl_2 (50 ml), and malonyl dichloride (0.65 ml, 67 mmol). CC (SiO_2/CH_2Cl_2) gave **6** (1.71 g, 70%). Orange-yellow oil. R_f (CH_2Cl_2): 0.57. $[\alpha]_D^{22} = +88.5$ ($c = 0.92$, $CHCl_3$). IR (neat): 3088*w*, 3064*w*, 3032*w*, 2960*m*, 2935*w*, 2872*w*, 1750*s*, 1734*s*, 1605*w*, 1584*w*, 1495*w*, 1455*w*, 1338*w*, 1331*w*, 1263*m*, 1202*w*, 1150*m*, 1101*w*, 1055*w*, 1022*w*, 979*w*, 760*w*, 699*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.40–7.30 (*m*, 10 H); 5.90 (*dd*, $J = 7.8$, 6.2, 2 H); 3.45 (*s*, 2 H); 2.04–1.75 (*m*, 4 H); 1.48–1.28 (*m*, 4 H); 0.98 (*t*, $J = 7.3$, 6 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 166.15; 140.55; 128.78; 128.32; 126.90; 77.35; 42.27; 38.46; 18.82; 13.9. FAB-MS: 369.2 (8, MH^+), 133.1 (100, $[PhC_4H_8]^+$).

*Bis[(*R*)-1-phenylbutyl] 1,2-Methano[70]fullerene-71,71-dicarboxylate* (**7**). A soln. of C_{70} (202 mg, 0.24 mmol) in dry PhMe (210 ml) was sonicated and purged with Ar, after which **6** (97 mg, 0.264 mmol), I_2 (67 mg, 0.264 mmol), and DBU (109 mg, 721 mmol), each dissolved in PhMe, were added. The soln. was stirred at r.t. overnight. After concentration, the mixture was chromatographed (SiO_2; PhMe/hexane 1:1) to give **7**

(110 mg, 40%). R_f (PhMe/hexane 1:1): 0.50. UV/VIS (CH_2Cl_2): 672 (sh, 900), 606 (sh, 3100), 542 (sh, 9300), 460 (20300), 403 (18000), 370 (22100), 353 (23100), 326 (sh, 24900), 265 (sh, 98200). IR (KBr): 2952*m*, 2924*s*, 2854*w*, 1737*m*, 1493*w*, 1453*w*, 1427*m*, 1377*w*, 1267*w*, 1225*s*, 1176*w*, 1160*w*, 1135*w*, 1092*w*, 1053*w*, 1029*w*, 960*w*, 928*w*, 795*w*, 756*w*, 695*s*, 672*w*, 578*m*, 532*w*, 458*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.44–7.21 (*m*, 10 H); 6.01 (*t*, *J* = 6.9, 2 H); 2.11–2.07 (*m*, 2 H); 1.94–1.88 (*m*, 2 H); 1.50–1.35 (*m*, 4 H); 0.99 (*t*, *J* = 7.3, 3 H); 0.94 (*t*, *J* = 7.3, 3 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 162.75 (C=O); 162.70 (C=O); 155.15; 154.98; 151.34; 151.26; 151.15 (2×); 150.70; 150.67; 150.56 (2×); 149.29; 149.21 (2×); 149.07; 149.03; 148.65; 148.53; 148.49 (2×); 148.45 (2×); 148.40; 148.37; 147.52; 147.50 (3×); 147.27 (2×); 146.97 (2×); 146.43; 145.89 (2×); 145.86; 145.81; 144.88; 144.74; 143.91 (2×); 143.81; 143.77; 143.47 (2×); 142.87; 142.77; 142.52; 142.09; 142.01; 141.55; 141.50; 140.67; 140.56; 139.00 (arom. C); 138.92 (arom. C); 136.90; 136.61; 133.52; 133.47; 132.80; 132.78; 130.87; 130.86; 130.84; 130.77 (2×); 130.72; 128.62 (arom. CH); 128.60 (arom. CH); 128.53 (arom. CH); 128.49 (arom. CH); 127.24 (arom. CH); 127.17 (arom. CH); 79.78 (Ph*C*HO); 79.76 (Ph*C*HO); 66.81 (fullerene sp^3-C); 66.14 (fullerene sp^3-C); 37.82 (CH_2); 37.81 (CH_2); 37.44 (methano bridge); 18.90 (CH_2); 18.87 (CH_2); 13.84 (Me); 13.81 (Me). MALDI-TOF-MS (DHB): 1206.2 (83, M^-, $^{12}C_{92}{}^{13}CH_{26}O_4$; calc. 1207.2), 1030.4 (8), 880.5 (14), 852.5 (100), 839.4 (45, C_{70}^-).

*Synthesis of Bis-adducts (*R,R,R,R,^{f}A*)*-**1**, *(*R,R,R,R,^{f}C*)*-**2**, *(*R,R,R,R,^{f}A*)*-**3**, *(*R,R,R,R,^{f}C*)*-**4**, *and (*R,R,R,R*)*-**5**. A soln. of C_{70} (89 mg, 0.106 mmol) in dry PhMe (100 ml) was purged with Ar for 30 min, after which I_2 (48 mg, 0.191 mmol), **6** (71 mg, 0.191 mmol), and DBU (81 mg, 0.532 mmol), each dissolved in PhMe, were added. The mixture was stirred overnight. CC (SiO_2; PhMe/hexane 1:1) gave **7** (6 mg, 4%) and a mixture of bis-adducts (*R*,*R*,*R*,*R*)-**1** – (*R*,*R*,*R*,*R*)-**5** (90 mg, 54%).

The bis-adduct fraction was separated by prep. HPLC (SiO_2). An average of 9 mg of bis-adduct, dissolved in PhMe/hexane 1:1, was injected onto the column and eluted as previously described for (*S*,*S*,*S*,*S*)-**1** – (*S*,*S*,*S*,*S*)-**5** [4]. *Fr. 1* (7 mg, 4%), *Fr. 2* (6 mg, 4%), *Fr. 3* (30 mg, 18%), *Fr. 4* (35 mg, 21%), and *Fr. 5* (15 mg, 9%) were isolated and characterized. Drying of the samples at *ca.* 10^{-7} Torr did not remove small amounts of hexane, which could still be identified by NMR after prolonged drying.

*Tetrakis[(*R*)-1-phenylbutyl] (*^{f}A*)- 1,2:67,68-Bis(methano)[70]fullerene-71,71,72,72-tetracarboxylate* ((*R*,*R*,*R*,*R*,^{f}*A*)-**3**). *Product of HPLC* Fr. 1*:* R_f (PhMe/hexane 1:1): 0.19. UV/VIS (CH_2Cl_2): 687 (sh, 900); 637 (sh, 1600); 560 (sh, 5400); 518 (sh, 9000); 469 (14900); 466 (14900), 462 (14900), 445 (15000), 402 (14200), 364 (14100), 343 (15600), 284 (sh, 48500), 258 (sh, 88800). CD (CH_2Cl_2): 692 ($\Delta\varepsilon$ = 22), 590 (9), 533 (15), 465 (–72), 399 (42), 377 (46), 358 (70), 314 (–103), 279 (41), 256 (–50), 233 (86). IR (KBr): 2956*m*, 2924*s*, 2855*m*, 1730*m*, 1494*w*, 1462*w*, 1426*w*, 1379*w*, 1271*m*, 1244*w*, 1225*w*, 1165*w*, 1121*w*, 1097*w*, 1073*w*, 1029*w*, 965*w*, 930*w*, 795*w*, 757*w*, 740*w*, 697*m*, 673*w*, 581*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.47–7.14 (*m*, 20 H); 6.03–5.98 (*m*, 4 H); 2.14–2.07 (*m*, 4 H); 1.94–1.86 (*m*, 4 H); 1.52–1.22 (*m*, 8 H); 0.99 (*t*, *J* = 7.4, 6 H); 0.96 (*t*, *J* = 7.4, 6 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 162.85 (C=O); 162.65 (C=O); 156.14; 155.25; 151.85; 151.18; 150.31; 150.20; 148.90; 148.86; 148.24; 148.20; 147.91; 147.32; 146.88; 146.65; 143.95; 143.90; 143.16; 142.90; 142.68; 142.08; 141.58; 140.93; 140.57; 140.19; 139.21; 139.08 (arom. C); 138.99; 138.96 (arom. C); 137.25; 136.93; 133.52; 132.99; 132.48; 132.39; 130.51; 128.58 (arom. CH); 128.52 (arom. CH); 128.45 (arom. CH); 128.24 (arom. CH); 127.25 (arom. CH); 127.15 (arom. CH); 79.68 (Ph*C*HO); 79.65 (Ph*C*HO); 67.50 (fullerene sp^3-C); 66.74 (fullerene sp^3-C); 38.76 (CH_2); 37.86 (CH_2); 36.85 (methano bridge); 18.91 (CH_2); 18.88 (CH_2); 13.85 (Me); 13.82 (Me); a peak at 29.71 was assigned as impurity. MALDI-TOF-MS (DHB): 1573.0 (100, M^-, $^{12}C_{115}{}^{13}CH_{52}O_8$; calc. 1573.4), 1397.1 (7).

*Tetrakis[(*R*)-1-phenylbutyl] (*^{f}C*)- 1,2:67,68-Bis(methano)[70]fullerene-71,71,72,72-tetracarboxylate* ((*R*,*R*,*R*,*R*,^{f}*C*)-**4**). *Product of HPLC* Fr. 2*:* R_f (PhMe/hexane 1:1): 0.19. UV/VIS (CH_2Cl_2): 690 (sh, 800), 642 (sh, 1500), 560 (sh, 6300), 519 (sh, 10500), 468 (17800), 462 (17800), 460 (17800), 450 (17900), 404 (17000), 366 (16900), 310 (sh, 30500), 286 (sh, 55800), 258 (sh, 106300). CD (CH_2Cl_2): 727 ($\Delta\varepsilon$ = 7), 698 (1), 638 (10), 610 (7), 601 (7), 530 (–10), 466 (83), 399 (–45), 377 (–49), 358 (–77), 314 (115), 291 (13), 279 (–38), 258 (47), 236 (–109). IR (KBr): 2956*m*, 2924*s*, 2853*m*, 1737*s*, 1655*w*, 1635*w*, 1578*w*, 1558*w*, 1495*w*, 1448*m*, 1426*w*, 1414*w*, 1377*w*, 1313*w*, 1261*m*, 1243*m*, 1224*s*, 1165*w*, 1137*w*, 1096*w*, 1049*w*, 1027*w*, 929*w*, 795*w*, 756*w*, 739*w*, 695*m*, 670*w*, 580*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.46–7.14 (*m*, 20 H); 6.02–5.98 (*m*, 4 H); 2.23–2.07 (*m*, 4 H); 1.94–1.85 (*m*, 4 H); 1.51–1.20 (*m*, 8 H); 1.00 (*t*, *J* = 7.4, 6 H); 0.95 (*t*, *J* = 7.4, 6 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 162.79 (C=O); 162.70 (C=O); 155.97; 155.42; 151.87; 151.12; 150.29; 150.27; 148.89; 148.82; 148.31; 148.28; 147.81; 147.32; 146.85; 146.70; 143.99; 143.84; 143.09; 142.92; 142.69; 142.18; 141.67; 140.56; 140.52; 140.26; 139.33; 139.14; 139.06 (arom. C); 139.00 (arom. C); 137.52; 136.68; 133.57; 132.96; 132.49; 132.27; 130.63; 128.55 (arom. CH); 128.52 (arom. CH); 128.45 (arom. CH); 128.24 (arom. CH); 127.23 (arom. CH); 127.13 (arom. CH); 79.68 (Ph*C*HO); 79.66 (Ph*C*HO); 67.51 (fullerene sp^3-C); 66.76 (fullerene sp^3-C); 37.89

(CH_2); 37.84 (CH_2); 36.86 (methano bridge); 18.90 (CH_2); 18.86 (CH_2); 13.85 (Me); 13.81 (Me); a peak at 29.71 was assigned as impurity. MALDI-TOF-MS (DHB): 1573.0 (100, M^-, $^{12}C_{115}{}^{13}CH_{52}O_8$; calc. 1573.4), 1397.3 (9).

*Tetrakis[(*R*)-1-phenylbutyl] (*^{f}*C)- 1,2:56,57-Bis(methano)[70]fullerene-71,71,72,72-tetracarboxylate* ((*R*,*R*,*R*,*R*,^{f}*C*)-**2**). *Product of HPLC* Fr. 3: R_f (PhMe/hexane 1:1): 0.19. UV/VIS (CH_2Cl_2): 659 (sh, 1600), 519 (sh, 13900), 463 (20200), 433 (21100), 398 (20600), 372 (sh, 17900), 332 (sh, 24900), 245 (sh, 124800). CD (CH_2Cl_2): 725 ($\Delta\varepsilon = 19$), 646 (8), 621 (13), 576 (−9), 539 (−33), 487 (58), 463 (18), 454 (22), 442 (12), 426 (22), 407 (−3), 387 (−26), 367 (−63), 350 (−33), 319 (67), 293 (11), 286 (17), 259 (−103), 235 (89). IR (KBr): 2956*m*, 2922*s*, 2853*m*, 1743*s*, 1636*w*, 1494*w*, 1455*m*, 1424*w*, 1379*w*, 1333*w*, 1309*w*, 1271*m*, 1236*s*, 1179*w*, 1163*w*, 1094*w*, 1050*w*, 1029*w*, 1000*w*, 930*w*, 794*w*, 758*w*, 740*w*, 726*w*, 695*s*, 670*w*, 655*w*, 580*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.45–7.22 (*m*, 20 H); 6.06–6.01 (*m*, 4 H); 2.13–2.09 (*m*, 4 H); 1.94–1.91 (*m*, 4 H); 1.55–1.34 (*m*, 8 H); 1.02 (*t*, *J* = 7.4, 6 H); 0.95 (*t*, *J* = 7.4, 6 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 162.80 (C=O); 162.76 (C=O); 155.56; 154.87; 152.74; 152.06; 151.61; 151.17; 150.43; 149.83; 148.74; 147.40; 146.27; 146.19; 146.16; 144.81; 144.70; 144.37; 144.32; 143.41; 143.07; 142.40; 142.28; 142.07; 141.31; 141.29; 140.30 (2×); 139.00 (arom. C); 138.97 (arom. C); 137.78; 137.49; 135.78; 132.88; 132.62; 131.29; 131.00; 128.57 (arom. CH); 128.53 (arom. CH); 128.49 (arom. CH); 128.42 (arom. CH); 127.19 (arom. CH); 127.17 (arom. CH); 79.67 (2×) (Ph*C*HO); 67.10 (fullerene sp^3-C); 66.65 (fullerene sp^3-C); 38.22 (methano bridge); 37.84 (CH_2); 37.81 (CH_2); 18.89 (CH_2); 18.84 (CH_2); 13.83 (Me); 13.78 (Me); a peak at 29.67 was assigned as impurity. MALDI-TOF-MS (DHB): 1573.1 (100, M^-, $^{12}C_{115}{}^{13}CH_{52}O_8$; calc. 1573.4), 1396.8 (7).

*Tetrakis[(*R*)-1-phenylbutyl] (*^{f}*A)- 1,2:56,57-Bis(methano)[70]fullerene-71,71,72,72-tetracarboxylate* ((*R*,*R*,*R*,*R*,^{f}*A*)-**1**). *Product of HPLC* Fr. 4: R_f (PhMe/hexane 1:1): 0.19. UV/VIS (CH_2Cl_2): 659 (sh, 1500), 525 (sh, 13800), 462 (20800), 435 (21700), 398 (21600), 373 (sh, 18800), 332 (sh, 26000), 246 (sh, 129300). CD (CH_2Cl_2): 701 ($\Delta\varepsilon = 11$), 673 (8), 646 (13), 621 (6), 578 (22), 540 (41), 487 (−53), 463 (−17), 455 (−20), 442 (−11), 427 (−19), 408 (3), 391 (21), 368 (60), 350 (31), 318 (−64), 293 (−8), 286 (−14), 259 (101), 233 (−99). IR (KBr): 2955*m*, 2924*s*, 2855*m*, 1741*s*, 1654*w*, 1558*w*, 1496*w*, 1457*w*, 1426*w*, 1376*w*, 1272*m*, 1234*s*, 1178*w*, 1160*w*, 1137*w*, 1094*w*, 1051*w*, 1029*w*, 931*w*, 794*w*, 758*w*, 740*w*, 696*m*, 670*w*, 579*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.45–7.17 (*m*, 20 H); 6.03–6.00 (*m*, 4 H); 2.11–2.09 (*m*, 4 H); 1.93–1.90 (*m*, 4 H); 1.46–1.36 (*m*, 8 H); 0.98 (*t*, *J* = 7.4, 6 H); 0.95 (*t*, *J* = 7.4, 6 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 162.82 (C=O); 162.68 (C=O); 155.40; 155.01; 152.79; 152.14; 151.58; 151.12; 150.47; 149.72; 148.86; 147.37; 146.33; 146.22; 146.18; 145.02; 144.72; 144.40; 144.22; 143.37; 143.10; 142.15; 142.12; 142.04; 141.30; 141.23; 140.44; 140.35; 139.05 (arom. C); 138.93 (arom. C); 137.79; 137.47; 135.73; 132.86; 132.78; 131.15; 131.01; 128.92 (arom. CH); 128.58 (arom. CH); 128.48 (arom. CH); 127.67 (arom. CH); 127.21 (arom. CH); 127.14 (arom. CH); 79.72 (Ph*C*HO); 79.66 (Ph*C*HO); 67.10 (fullerene sp^3-C); 66.64 (fullerene sp^3-C); 38.24 (methano bridge); 37.84 (CH_2); 37.81 (CH_2); 18.64 (CH_2); 18.45 (CH_2); 13.80 (Me); 13.77 (Me); a peak at 29.66 was assigned as impurity. MALDI-TOF-MS (DHB): 1572.9 (100, M^-, $^{12}C_{115}{}^{13}CH_{52}O_8$; calc. 1573.4), 1397.3 (14).

*Tetrakis[(*R*)-1-phenylbutyl] 1,2:41,58-Bis(methano)[70]fullerene-71,71,72,72-tetracarboxylate* ((*R*,*R*,*R*,*R*)-**5**). *Product of HPLC* Fr. 5: R_f (PhMe/hexane 1:1): 0.19. UV/VIS (CH_2Cl_2): 663 (sh, 1600), 533 (sh, 10100), 475 (19200), 422 (sh, 18500), 401 (20800), 307 (sh, 33600), 269 (91300), 243 (sh, 120500). CD (CH_2Cl_2): 295 ($\Delta\varepsilon = 1$), 275 (8). IR (KBr): 2954*m*, 2923*s*, 2851*m*, 1742*s*, 1654*w*, 1638*w*, 1560*w*, 1538*w*, 1494*w*, 1455*m*, 1424*w*, 1413*w*, 1375*w*, 1312*w*, 1262*s*, 1230*s*, 1220*s*, 1174*m*, 1138*w*, 1093*m*, 1054*w*, 1029*w*, 1001*w*, 933*w*, 911*w*, 842*w*, 795*w*, 757*w*, 737*w*, 726*w*, 697*m*, 668*w*, 621*w*, 577*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.44–7.16 (*m*, 20 H); 6.04–6.01 (*m*, 4 H); 2.13–2.09 (*m*, 4 H); 1.94–1.89 (*m*, 4 H); 1.54–1.33 (*m*, 8 H); 0.99 (*t*, *J* = 7.4, 6 H); 0.95 (*t*, *J* = 7.4, 6 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 162.87 (C=O); 162.84 (C=O); 154.43; 154.25; 152.48; 152.41; 151.37; 149.81; 149.68; 149.20; 149.18; 148.69; 148.53; 147.36; 147.33; 142.68; 142.64; 142.45; 142.39; 142.05; 142.00; 141.96; 141.87; 141.81; 141.49; 141.44; 139.02 (arom. C); 138.96 (arom. C); 137.31; 137.00; 136.65; 135.77; 135.20; 134.41; 132.57; 131.54; 131.10; 128.92 (arom. CH); 128.57 (arom. CH); 128.48 (arom. CH); 127.66 (arom. CH); 127.22 (arom. CH); 127.14 (arom. CH); 79.72 (Ph*C*HO); 79.69 (Ph*C*HO); 66.20 (fullerene sp^3-C); 65.94 (fullerene sp^3-C); 37.85 (CH_2); 37.81 (CH_2); 36.83 (methano bridge); 18.87 (CH_2); 18.85 (CH_2); 13.80 (Me); 13.77 (Me); a peak at 29.66 was assigned as impurity. MALDI-TOF-MS (DHB): 1572.8 (100, M^-, $^{12}C_{115}{}^{13}CH_{52}O_8$; calc. 1573.4), 1396.7 (11).

*Reaction of Bis-adducts (*S,S,S,S,^{f}*C)-***1***, (*R,R,R,R,^{f}*A)-***1** *and (*S,S,S,S,^{f}*A)-***2***, (*R,R,R,R,^{f}*C)-***2** *with Diethyl 2-Bromomalonate. 72,72,73,73-Tetraethyl 71,71,74,74-Tetrakis[(*S*)-1-phenylbutyl] (*^{f}*C)-1,2:31,32:54,55:59,60-Tetrakis(methano)[70]fullerene-71,71,72,72,73,73,74,74-octacarboxylate* ((*S*,*S*,*S*,*S*,^{f}*C*)-**9**). A soln. of (*S*,*S*,*S*,*S*,^{f}*A*)-**2** (Fr. III [4]; 36 mg, 0.022 mmol) in CCl_4 (50 ml) was stirred at r.t., after which diethyl 2-bromomalonate (44 mg, 0.182 mmol) and DBU (28 mg, 0.182 mmol) were added. After 2 and 3 d, another 8 mg of diethyl 2-bromomalonate (0.035 mmol) as well as 5 mg of DBU (0.035 mmol) were added, resp. After 4.5 d, the

concentrated mixture was chromatographed (SiO_2; CH_2Cl_2/hexane 7:3 → CH_2Cl_2 → CH_2Cl_2/MeOH 98:2) to give (*S,S,S,S,*^{f}*C*)-**9** (5 mg, 12%) in addition to two fractions containing higher adducts.

*(*S,S,S,S,^{f}C*)-**9**: R_f (CH_2Cl_2/hexane 7:3): 0.43. UV/VIS (CH_2Cl_2): 628 (3200), 578 (sh, 3900), 522 (7100), 513 (sh, 7200), 487 (sh, 10700), 450 (sh, 13100), 383 (19200), 299 (sh, 41500), 256 (92700), 237 (sh, 96600). CD (CH_2Cl_2): 664 ($\Delta\varepsilon = -4$), 628 (12), 580 (−2), 525 (−18), 499 (5), 460 (73), 396 (−27), 377 (1), 367 (−3), 345 (35), 333 (48), 303 (−85), 282 (−23), 271 (−53). IR (KBr): 3063*w*, 3033*w*, 2955*s*, 2925*s*, 2862*m*, 1744*s*, 1724*m*, 1650*w*, 1495*w*, 1457*m*, 1381*w*, 1364*w*, 1273*m*, 1233*s*, 1163*w*, 1093*m*, 1070*w*, 1019*w*, 969*w*, 933*w*, 857*w*, 791*w*, 761*w*, 737*w*, 724*w*, 699*m*, 648*w*, 580*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.48–7.23 (*m*, 20 H); 6.01–5.95 (*m*, 4 H); 4.56 (*q*, *J* = 7.1, 4 H); 4.23–4.20 (*m*, 4 H); 2.07–2.00 (*m*, 4 H); 1.9–1.76 (*m*, 4 H); 1.56–1.20 (*m*, 8 H); 1.50 (*t*, *J* = 7.1, 6 H); 1.20 (*t*, *J* = 7.1, 6 H); 0.99 (*t*, *J* = 7.4, 6 H); 0.91 (*t*, *J* = 7.4, 6 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 164.33 (C=O); 164.00 (C=O); 162.84 (C=O); 162.81 (C=O); 156.24; 152.06; 151.90; 149.28; 146.53; 146.27; 146.12; 145.82; 145.20; 144.30; 143.93; 143.56; 143.47; 143.35; 143.08; 142.45; 141.69; 141.43; 140.90; 140.84; 140.26; 139.08 (arom. C); 139.06 (arom. C); 138.99; 138.50; 137.48; 137.04; 136.18; 134.95; 134.55; 133.78; 132.80; 129.85; 128.54 (arom. CH); 128.48 (arom. CH); 128.45 (arom. CH); 128.39 (arom. CH); 127.20 (arom. CH); 127.14 (arom. CH); 79.53 (Ph*C*HO); 79.50 (Ph*C*HO); 69.17 (fullerene sp^3-C); 68.17 (fullerene sp^3-C); 67.88 (fullerene sp^3-C); 64.47 (CH_2); 64.00 (CH_2); 63.20 (CH_2); 62.78 (CH_2); 40.76 (methano bridge); 40.36 (methano bridge); 38.75 (methano bridge); 38.03 (methano bridge); 37.88 (2×) (CH_2); 18.85 (CH_2); 18.81 (CH_2); 14.22 (Me); 13.93 (Me); 13.82 (Me); 13.76 (CH_3); a peak at 29.69 was assigned as impurity. MALDI-TOF-MS (DHB): 1889.1 (100, M^-, $^{12}C_{129}{}^{13}CH_{72}O_{16}$; calc. 1889.5), 1713.2 (15).

*72,72,73,73-Tetraethyl 71,71,74,74-Tetrakis[(*S*)-1-phenylbutyl] (*^{f}A*)-1,2:31,32:54,55:59,60-Tetrakis(methano)-[70]fullerene-71,71,72,72,73,73,74,74-octacarboxylate* ((*S,S,S,S,*^{f}*A*)-**8**). As described above, (*S,S,S,S,*^{f}*C*)-**1** (Fr. IV [4]; 35 mg, 0.022 mmol), diethyl 2-bromomalonate (42 mg, 0.176 mmol), and DBU (27 mg, 0.176 mmol) reacted to give (*S,S,S,S,*^{f}*A*)-**8** (6 mg, 15%) in addition to two fractions containing higher adducts.

*(*S,S,S,S,^{f}A*)-**8**: R_f (CH_2Cl_2/hexane 7:3): 0.43. UV/VIS (CH_2Cl_2): 627 (3000), 578 (sh, 3600), 522 (6600), 513 (sh, 6700), 487 (sh, 9700), 450 (sh, 12100), 383 (17800), 299 (sh, 38800), 257 (85700), 237 (sh, 89300). CD (CH_2Cl_2): 665 ($\Delta\varepsilon = 16$), 629 (1), 611 (6), 557 (18), 535 (19), 525 (21), 499 (−1), 460 (−63), 395 (27), 376 (3), 365 (6), 346 (−25), 333 (−39), 303 (83), 282 (24), 271 (51), 251 (−53). IR (KBr): 3066*w*, 3035*w*, 2956*s*, 2919*s*, 2851*m*, 1744*s*, 1724*m*, 1645*w*, 1495*w*, 1455*w*, 1381*w*, 1366*w*, 1272*w*, 1232*s*, 1178*w*, 1163*w*, 1093*m*, 1073*w*, 1021*w*, 966*w*, 935*w*, 857*w*, 792*w*, 761*w*, 739*w*, 722*w*, 697*m*, 669*w*, 582*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.43–7.19 (*m*, 20 H); 6.00 (*t*, *J* = 6.8, 2 H); 5.95 (*t*, *J* = 7.0, 2 H); 4.56 (*q*, *J* = 7.2, 4 H); 4.25–4.19 (*m*, 4 H); 2.08–2.06 (*m*, 4 H); 1.90–1.86 (*m*, 4 H); 1.51–1.12 (*m*, 8 H); 1.50 (*t*, *J* = 7.1, 6 H); 1.20 (*t*, *J* = 7.1, 6 H); 0.95 (*t*, *J* = 7.3, 6 H); 0.95 (*t*, *J* = 7.2, 6 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 164.32 (C=O); 164.01 (C=O); 162.91 (C=O); 162.72 (C=O); 156.34; 152.14; 151.83; 149.26; 146.44; 146.37; 146.08; 145.93; 145.28; 145.24; 144.20; 143.91; 143.69; 143.59; 143.47; 143.06; 142.15; 141.67; 141.34; 140.97; 140.34; 139.12 (arom. C); 139.04 (arom. C); 138.49; 137.44; 136.99; 136.19; 134.72; 134.71; 134.02; 132.67; 130.85; 129.86; 128.81 (arom. CH); 128.53 (arom. CH); 128.42 (arom. CH); 128.32 (arom. CH); 127.22 (arom. CH); 127.11 (arom. CH); 79.59 (Ph*C*HO); 79.48 (Ph*C*HO); 69.17 (fullerene sp^3-C); 68.18 (2×, fullerene sp^3-C); 67.94 (fullerene sp^3-C); 64.50 (CH_2); 64.00 (CH_2); 63.19 (CH_2); 62.78 (CH_2); 40.80 (methano bridge); 40.43 (methano bridge); 38.79 (methano bridge); 38.26 (methano bridge); 37.91 (CH_2); 37.86 (CH_2); 18.85 (CH_2); 18.83 (CH_2); 14.23 (Me); 13.93 (Me); 13.79 (2×) (Me); a peak at 29.69 was assigned as impurity. MALDI-TOF-MS (DHB): 1889.1 (100, M^-, $^{12}C_{129}{}^{13}CH_{72}O_{16}$; calc. 1889.5), 1712.9 (24).

*72,72,73,73-Tetraethyl 71,71,74,74-Tetrakis[(*R*)-1-phenylbutyl] (*^{f}A*)-1,2:31,32:54,55:59,60-Tetrakis(methano)-[70]fullerene-71,71,72,72,73,73,74,74-octacarboxylate* ((*R,R,R,R,*^{f}*A*)-**9**). As described above, (*R,R,R,R,*^{f}*C*)-**2** (Fr. 3; 28 mg, 0.017 mmol), diethyl 2-bromomalonate (17 mg, 0.070 mmol) and DBU (11 mg, 0.070 mmol) reacted to give (*R,R,R,R,*^{f}*A*)-**9** (11 mg, 34%) in addition to two fractions containing higher adducts.

*(*R,R,R,R,^{f}A*)-**9**: R_f (CH_2Cl_2/hexane 7:3): 0.43. UV/VIS (CH_2Cl_2): 629 (3600), 578 (sh, 4200), 525 (7700), 487 (sh, 10800), 450 (sh, 15000), 381 (22300), 299 (sh, 46900), 257 (102900), 237 (sh, 105200). CD (CH_2Cl_2): 666 ($\Delta\varepsilon = 14$), 648 (9), 630 (5), 599 (10), 589 (9), 532 (14), 524 (15), 500 (1), 460 (−40), 396 (18), 377 (4), 366 (6), 346 (−16), 333 (−25), 303 (54), 282 (17), 271 (34). IR (KBr): 3065*w*, 3029*w*, 2954*s*, 2924*s*, 2855*s*, 1742*s*, 1582*w*, 1559*w*, 1541*w*, 1497*w*, 1454*m*, 1378*w*, 1367*w*, 1335*w*, 1232*s*, 1179*w*, 1164*w*, 1120*w*, 1092*m*, 1069*w*, 1021*w*, 966*w*, 934*w*, 857*w*, 792*w*, 760*w*, 736*w*, 697*m*, 667*w*, 649*w*, 580*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.38–7.14 (*m*, 20 H); 6.00 (*t*, *J* = 7.0, 2 H); 5.95 (*t*, *J* = 6.9, 2 H); 4.56 (*q*, *J* = 7.1, 4 H); 4.26–4.16 (*m*, 4 H); 2.12–2.00 (*m*, 4 H); 1.93–1.81 (*m*, 4 H); 1.67–1.18 (*m*, 8 H); 1.50 (*t*, *J* = 7.2, 6 H); 1.20 (*t*, *J* = 7.1, 6 H); 0.99 (*t*, *J* = 7.4, 6 H); 0.91 (*t*, *J* = 7.4, 6 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 164.35 (C=O); 164.02 (C=O); 162.86 (C=O); 162.83 (C=O); 156.26; 152.08; 151.92; 149.30; 146.55; 146.29; 146.14; 145.84; 145.22; 144.32; 143.95; 143.58; 143.48; 143.37; 143.10; 142.47; 141.71; 141.44; 140.92; 140.28; 139.10 (arom. C); 139.08 (arom. C); 139.01; 138.52; 137.50;

137.06; 136.20; 134.97; 134.57; 133.80; 132.82; 129.87; 129.05; 128.56 (arom. CH); 128.50 (arom. CH); 128.47 (arom. CH); 128.41 (arom. CH); 127.22 (arom. CH); 127.16 (arom. CH); 79.55 (Ph*C*HO); 79.52 (Ph*C*HO); 69.19 (fullerene sp^3-C); 68.19 (fullerene sp^3-C); 67.90 (2×, fullerene sp^3-C); 64.49 (CH_2); 64.02 (CH_2); 63.22 (CH_2); 62.80 (CH_2); 40.78 (methano bridge); 40.38 (methano bridge); 38.77 (methano bridge); 38.05 (methano bridge); 37.90 (CH_2); 37.87 (CH_2); 18.88 (CH_2); 18.83 (CH_2); 14.25 (Me); 13.95 (Me); 13.84 (Me); 13.78 (Me); a peak at 29.71 was assigned as impurity. MALDI-TOF-MS (DHB): 1888.5 (100, M^-, $^{12}C_{129}{}^{13}CH_{72}O_{16}$; calc. 1889.5).

*72,72,73,73-Tetraethyl 71,71,74,74-Tetrakis[(*R*)-1-phenylbutyl] (*^{f}*C)-1,2 : 31,32 : 54,55 : 59,60-Tetrakis(methano)-[70]fullerene-71,71,72,72,73,73,74,74-octacarboxylate* ((*R*,*R*,*R*,*R*,^{f}*C*)-**8**). As described above, (*R*,*R*,*R*,*R*,^{f}*A*)-**1** (Fr. 4; 29 mg, 0.018 mmol), diethyl 2-bromomalonate (33 mg, 0.144 mmol) and DBU (22 mg, 0.144 mmol) reacted to give (*R*,*R*,*R*,*R*,^{f}*C*)-**8** (13 mg, 37%) in addition to two fractions containing higher adducts.

*(*R,R,R,R,^{f}*C)-**8**: R_f (CH_2Cl_2/hexane 7:3): 0.43. UV/VIS (CH_2Cl_2): 629 (3400), 578 (sh, 3900), 525 (7500), 488 (sh, 9900), 450 (sh, 13900), 382 (21700), 299 (sh, 46300), 257 (102400), 236 (sh, 106000). CD (CH_2Cl_2): 664 ($\Delta\varepsilon = -8$), 626 (9), 582 (−3), 567 (−8), 525 (−19), 499 (6), 460 (82), 396 (−30), 376 (−1), 366 (−4), 346 (34), 333 (49), 303 (−96), 282 (−28), 271 (−56), 252 (64). IR (KBr): 3063*w*, 3032*w*, 2957*m*, 2926*s*, 2868*w*, 2831*w*, 1744*s*, 1684*w*, 1637*w*, 1559*w*, 1539*w*, 1520*w*, 1506*w*, 1496*w*, 1463*w*, 1454*m*, 1384*w*, 1367*w*, 1333*w*, 1271*m*, 1232*s*, 1178*w*, 1161*w*, 1094*m*, 1069*w*, 1021*w*, 968*w*, 932*w*, 910*w*, 857*w*, 792*w*, 738*w*, 723*w*, 698*m*, 668*w*, 649*w*, 581*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.43–7.19 (*m*, 20 H); 6.00 (*t*, *J* = 6.9, 2 H); 5.95 (*t*, *J* = 7.0, 2 H); 4.56 (*q*, *J* = 7.1, 4 H); 4.25–4.17 (*m*, 4 H); 2.11–2.01 (*m*, 4 H); 1.92–1.83 (*m*, 4 H); 1.56–1.18 (*m*, 8 H); 1.50 (*t*, *J* = 7.2, 6 H); 1.20 (*t*, *J* = 7.1, 6 H); 0.95 (*t*, *J* = 7.4, 6 H); 0.95 (*t*, *J* = 7.3, 6 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 164.32 (C=O); 164.00 (C=O); 162.90 (C=O); 162.71 (C=O); 156.34; 152.13; 151.82; 149.25; 146.44; 146.36; 146.07; 145.92; 145.27; 144.20; 143.90; 143.68; 143.58; 143.46; 143.06; 142.15; 141.66; 141.34; 140.96; 140.33; 139.12 (arom. C); 139.11 (arom. C); 139.03; 138.48; 137.44; 136.98; 136.18; 134.71; 134.70; 134.01; 132.67; 129.85; 128.53 (arom. CH); 128.52 (arom. CH); 128.41 (arom. CH); 128.31 (arom. CH); 127.22 (arom. CH); 127.10 (arom. CH); 79.59 (Ph*C*HO); 79.48 (Ph*C*HO); 69.20 (fullerene sp^3-C); 67.91 (fullerene sp^3-C); 64.49 (CH_2); 63.99 (CH_2); 63.19 (CH_2); 62.77 (CH_2); 40.79 (methano bridge); 40.43 (methano bridge); 38.81 (methano bridge); 37.90 (CH_2); 37.85 (CH_2); 18.85 (CH_2); 18.82 (CH_2); 14.23 (Me); 13.92 (Me); 13.78 (2×, Me); a peak at 29.68 was assigned as impurity. MALDI-TOF-MS (DHB): 1890.1 (100, M^-, $^{12}C_{129}{}^{13}CH_{72}O_{16}$; calc. 1889.5).

(±)-Tetraethyl 1,2 : 56,57-Bis(methano)[70]fullerene-71,71,72,72-tetracarboxylate ((±)-**13**). K_2CO_3 (dry, ≥ 99% from *Fluka*; 1.194 g, 8.638 mmol) was added to a soln. of (±)-**10** (150 mg, 0.108 mmol) in dry THF/EtOH 1:1 (100 ml), and the mixture was stirred at r.t. under Ar for 2 h. After filtration (SiO_2; CH_2Cl_2) and evaporation, CC (CH_2Cl_2/hexane 1:1), followed by recrystallization from CH_2Cl_2/pentane and drying at 25°/10^{-1} Torr, afforded (±)-**13** (114 mg, 91%). Black solid. R_f (CH_2Cl_2/hexane): 0.35. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.54 (*q*, *J* = 7.2, 4 H); 4.53 (*q*, *J* = 7.2, 4 H); 1.50 (*t*, *J* = 7.3, 6 H); 1.48 (*t*, *J* = 7.1, 6 H). FAB-MS: 1157.5 (100, M^+, $^{13}C^{12}C_{83}H_{20}O_8$; calc. 1157.1), 840.1 (84, $[C_{70}]^+$).

(±)-Tetraethyl 1,2 : 67,68-Bis(methano)[70]fullerene-71,71,72,72-tetracarboxylate ((±)-**14**). Reaction conditions and workup as indicated above for the synthesis of (±)-**13**. Conversion of (±)-**11** (50 mg, 0.036 mmol) in dry THF/EtOH 1:1 (50 ml) with K_2CO_3 (dry, ≥ 99% from *Fluka*; 398 mg, 2.879 mmol) afforded (±)-**14** (30 mg, 72%). Black solid. R_f (CH_2Cl_2/hexane): 0.35. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.52 (*q*, *J* = 7.1, 4 H); 4.51 (*q*, *J* = 7.1, 4 H); 1.48 (*t*, *J* = 7.1, 6 H); 1.47 (*t*, *J* = 7.1, 6 H). MALDI-TOF-MS (dithranol): 1156.7 (100, M^-, $^{13}C^{12}C_{83}H_{20}O_8$; calc. 1157.1).

Tetraethyl 1,2 : 41,58-Bis(methano)[70]fullerene-71,71,72,72-tetracarboxylate (**15**). Reaction conditions and workup as indicated above for the synthesis of (±)-**13**. Conversion of **12** (185 mg, 0.133 mmol) in dry THF/EtOH 1:1 (100 ml) with K_2CO_3 (dry, ≥ 99% from *Fluka*; 1.472 mg, 10.653 mmol) afforded **15** (121 mg, 79%). Black solid. R_f (CH_2Cl_2/hexane): 0.35. UV/VIS (CH_2Cl_2): 664 (1600), 629 (sh, 2100), 526 (sh, 10700), 489 (sh, 17800), 477 (18400), 417 (sh, 17500), 400 (19100), 364 (17300), 326 (sh, 19300), 269 (85900). IR (KBr): 2961*w*, 2922*w*, 2850*w*, 1747*s*, 1442*w*, 1424*w*, 1414*w*, 1386*w*, 1365*w*, 1295*w*, 1263*s*, 1233*s*, 1222*s*, 1175*m*, 1092*m*, 1065*w*, 1047*w*, 1015*m*, 857*w*, 795*w*, 725*w*, 702*w*, 668*w*, 576*w*, 540*w*, 539*w*, 454*w*, 421*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.55 (*q*, *J* = 7.1, 8 H); 1.51 (*t*, *J* = 7.0, 12 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 163.53 (C=O); 154.40; 152.54; 151.42; 149.91; 149.13; 148.72; 147.52; 142.75; 142.66; 142.17; 142.08; 141.95; 141.56; 137.42; 136.79; 135.24; 131.74; 131.22; 130.62; 66.29 (fullerene sp^3-C); 66.06 (fullerene sp^3-C); 63.40 (2×, CH_2); 36.64 (methano bridge); 14.22 (Me). FAB-MS: 1157.3 (83, M^+, $^{13}C^{12}C_{83}H_{20}O_8$; calc. 1157.1), 840.1 (100, $[C_{70}]^+$).

(±)-Octaethyl 1,2 : 31,32 : 54,55 : 59,60-Tetrakis(methano)[70]fullerene-71,71,72,72,73,73,74,74-octacarboxylate ((±)-**16**). Diethyl 2-bromomalonate (41 mg, 0.173 mmol) and DBU (26 mg, 0.173 mmol) in CCl_4 (4 ml) were added to a soln. of (±)-**13** (100 mg, 0.086 mmol) in CCl_4 (100 ml). Additional amounts of reagent and base were added after stirring at r.t. under Ar in the dark for 24 h (diethyl 2-bromomalonate: 41 mg, 0.173 mmol;

DBU: 26 mg, 0.173 mmol) and 48 h (diethyl 2-bromomalonate: 82 mg, 0.346 mmol; DBU: 52 mg, 0.346 mmol). After stirring for a total of 7 d, the reaction was terminated. Filtration (SiO_2; CH_2Cl_2) and evaporation, followed by CC (SiO_2; CH_2Cl_2/hexane 1:1 → CH_2Cl_2) afforded three brown fractions. Recrystallization from CH_2Cl_2/pentane and drying at 25°/10^{-1} Torr yielded, besides starting material (±)-**13** (2 mg, 2%), a mixture of tris-adducts (36 mg, 32%), and tetrakis-adduct (±)-**16** (58 mg, 45%). Black solid. R_f (CH_2Cl_2): 0.73. UV/VIS (CH_2Cl_2): 629 (4900), 578 (5300), 526 (sh, 9900), 487 (sh, 11700), 435 (18200), 380 (27800), 289 (sh, 66500), 256 (129100). IR (KBr): 2975*w*, 1743*s*, 1636*w*, 1464*w*, 1442*w*, 1388*w*, 1365w, 1233*s*, 1094*m*, 1017*m*, 856*w*, 791*w*, 724*w*, 704*w*, 649*w*, 581*w*, 530*w*, 511*w*, 460*w*, 424*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.59 (*q*, *J* = 7.1, 4 H); 4.51 (*q*, *J* = 7.1, 4 H); 4.47 (*q*, *J* = 7.1, 4 H); 4.26 (*q*, *J* = 7.2, 2 H); 4.25 (*q*, *J* = 7.1, 2 H); 1.51 (*t*, *J* = 7.2, 6 H); 1.48 (*t*, *J* = 7.2, 6 H); 1.44 (*t*, *J* = 7.2, 6 H); 1.23 (*t*, *J* = 7.0, 6 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 164.33 (C=O); 163.93 (C=O); 163.50 (C=O); 163.43 (C=O); 156.48; 152.19; 151.97; 149.44; 146.62; 146.46; 146.29; 145.94; 145.40; 144.38; 144.05; 143.83; 143.62; 143.60; 143.22; 142.57; 141.81; 141.56; 141.03; 140.42; 139.19; 138.56; 137.52; 137.18; 136.29; 135.04; 134.78; 134.04; 132.87; 129.85; 128.58; 69.25 (fullerene sp^3-C); 67.91 (fullerene sp^3-C); 64.55 (fullerene sp^3-C); 64.06 (fullerene sp^3-C); 63.24 (2×, CH_2); 63.19 (CH_2); 62.80; 40.82 (methano bridge); 40.23 (methano bridge); 14.19 (2×, Me); 14.15 (Me); 13.92 (Me). FAB-MS: 1473.4 (100, M^+, $^{13}C^{12}C_{97}H_{40}O_{16}$; calc. 1473.2), 840.0 (37, $[C_{70}]^+$).

*Conversion of (±)-***13** *to Higher C_{70} Adducts. i*) To a suspension of (±)-**13** (50 mg, 0.043 mmol) in Me_2SO (15 ml) was added diethyl 2-bromomalonate (83 mg, 0.346 mmol) and DBU (53 mg, 0.346 mmol) in Me_2SO (2 ml). After stirring at r.t. under Ar in the dark for 2 h, a homogenous solution had formed. The mixture was diluted with PhMe (300 ml), washed with H_2O (3 × 100 ml) and satd. NaCl soln. (3 × 100 ml), and dried ($MgSO_4$). After concentration, recrystallization from CH_2Cl_2/pentane, and drying at 25°/10^{-1} Torr yielded 66 mg of a mixture of higher C_{70} adducts. CC (SiO_2; CH_2Cl_2 → CH_2Cl_2/AcOEt 80:20) afforded six fractions. Repeated CC of these fractions (SiO_2-*H*; CH_2Cl_2 → CH_2Cl_2/AcOEt 95:5) gave six C_{70} adduct fractions (*Table*). *Fr. A-I:* tetrakis-adduct (±)-**16** (4 mg, 6%); *Fr. A-II:* pentakis-adduct(s) (5 mg, 7%); *Fr. A-III:* hexakis-adduct(s) (7 mg, 9%); *Fr. A-IV:* hexakis-adduct (±)-**22** (16 mg, 21%); *Fr. A-V:* heptakis-adduct(s) (10 mg, 12%); *Fr. A-VI:* heptakis-adduct(s) (3 mg, 3%).

(±)-Dodecaethyl 3,4:28,29:41,58:65,66-Tetrakis(methano)-7,8(8a):37,38(38a)-dihomo[70]fullerene-8a, 8a,38a,38a,71,71,72,72,73,73,74,74-dodecacarboxylate ((±)-**22**). *Product of* Fr. A-IV: Brown solid. R_f (CH_2Cl_2/AcOEt 98.5:1.5): 0.28. UV/VIS (CH_2Cl_2): 632 (sh, 3200), 533 (6800), 456 (sh, 12600), 431 (sh, 14800), 382 (22700), 293 (sh, 70600), 258 (116900). IR (KBr): 2978*w*, 2933*w*, 1744*s*, 1633*w*, 1463*w*, 1445*w*, 1389*w*, 1367*w*, 1296*m*, 1231*s*, 1093*m*, 1019*m*, 856*w*, 758*w*, 729*w*, 668*w*, 653*w*, 583*w*, 553*w*, 531*w*, 508*w*, 456*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.65–4.20 (*m*, 20 H); 4.06 (*q*, *J* = 7.1, 4 H); 1.55–1.30 (*m*, 24 H); 1.24 (*t*, *J* = 7.0, 6 H); 1.12 (*t*, *J* = 7.2, 6 H). ^{13}C-NMR (100.6 MHz, $CDCl_3$, *ca.* 40 mM [Cr(acac)$_3$]): 166.28 (C=O); 164.43 (C=O); 163.99 (C=O); 163.79 (C=O); 162.62 (C=O); 161.64 (C=O); 151.60; 149.91; 146.89; 146.79; 146.38; 145.43; 143.68; 143.61; 142.98; 142.18; 141.98; 141.81; 141.36; 141.09; 139.45; 137.61; 137.28; 137.12; 136.99; 135.51; 134.40; 133.80; 132.82; 131.69; 131.26; 130.76; 130.46; 129.59; 127.80; 109.34; 105.01; 66.30; 65.19; 65.06; 64.12; 63.86; 63.49 (CH_2); 63.14 (CH_2); 62.94 (CH_2); 62.76 (CH_2); 62.72 (CH_2); 62.57 (CH_2); 42.88 (methano bridge); 39.21 (methano bridge); 14.15 (Me); 14.03 (2×, Me); 13.93 (Me); 13.62 (Me). FAB-MS: 1789.5 (100, M^+), 1744.4 (27, $[M - C_2H_5O]^+$), 1631.4 (7, $[M - C_7H_{10}O_4]^+$), 840.0 (57, $[C_{70}]^+$). MALDI-TOF-MS (THA/diammonium citrate): 1788.9 (100, M^+, $^{13}C^{12}C_{111}H_{60}O_{24}$; calc. 1789.3), 1630.9 (87, $[M - C_7H_{10}O_4]^+$), 1472.2 (50, $[M - C_{14}H_{20}O_8]^+$), 1313.3 (17, $[M - C_{21}H_{30}O_{12}]^+$), 1156.2 (21, $[M - C_{28}H_{40}O_{16}]^+$).

ii) Application of the same reaction conditions (2.5 h) and the same workup as indicated above (synthesis of product *Fr. A-I – A-VI*) to the conversion of a homogeneous soln. of bis-adduct (±)-**13** (250 mg, 0.216 mmol) obtained by extended stirring in Me_2SO (45 ml), diethyl 2-bromomalonate (413 mg, 1.728 mmol), and DBU (263 mg, 1.728 mmol) afforded ten C_{70}-adduct fractions (*Table*). *Fr. B-I:* heptakis-adduct (16 mg, 5%); *Fr. B-II:* hexakis-adduct and heptakis-adduct (21 mg, 5%); *Fr. B-III:* heptakis-adducts (102 mg, 24%); *Fr. B-IV:* heptakis-adduct(s) (8 mg, 2%); *Fr. B-V:* octakis-adduct(s) (15 mg, 3%); *Fr. B-VI:* octakis-adduct (26 mg, 6%); *Fr. B-VII:* octakis-adduct (34 mg, 7%); *Fr. B-VIII:* octakis-adduct(s) (15 mg, 3%); *Fr. B-IX:* octakis-adduct(s) (15 mg, 3%); *Fr. B-X:* octakis-adduct (14 mg, 3%).

Tetradecaethyl Heptakis(methano)[70]fullerene-71,71,72,72,73,73,74,74,75,75,76,76,77,77-tetradecacarboxylate (C_1-symmetrical, position of the methano addends on the fullerene surface unknown). *Product of* Fr. B-I. Black solid. R_f (CH_2Cl_2/AcOEt 95:5): 0.51 UV/VIS (CH_2Cl_2): 631 (sh, 3400), 587 (5100), 539 (5700), 357 (sh, 29400), 325 (sh, 41500). IR (KBr): 2977*w*, 2936*w*, 1746*s*, 1632*w*, 1464*w*, 1444*w*, 1389*w*, 1367w, 1297*m*, 1231*s*, 1094*m*, 1019*m*, 856*w*, 725*w*, 581*w*, 533*w*, 456*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.65–4.00 (*m*, 28 H); 1.50–1.05 (*m*, 42 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 167.14 (C=O); 164.41 (C=O); 164.36 (C=O); 164.23 (2×) (C=O); 164.18 (C=O); 164.09 (C=O); 163.79 (C=O); 163.09 (C=O); 163.02 (C=O); 162.66 (C=O); 162.63 (C=O); 161.01

(C=O); 152.82; 148.73; 147.76; 147.56; 147.50; 147.39; 146.60; 146.12; 145.81; 144.70 (2×); 144.63; 144.50; 144.12; 143.83; 143.70; 143.27 (2×); 142.56; 142.35; 141.27; 141.20; 141.10; 140.84; 140.73; 140.38; 140.09; 139.87; 139.64; 139.27; 138.81; 137.65; 137.61; 137.26; 136.69; 136.47; 135.66; 134.57; 134.33; 133.69; 133.35; 133.22; 133.15; 132.97; 132.87; 132.78; 132.39; 131.93; 131.30; 130.20; 128.71; 125.37; 123.58; 123.38; 121.01; 115.01; 70.30; 67.47; 66.91; 66.34; 65.64; 64.61; 63.43; 63.18; 62.95; 62.90; 62.86; 62.83; 62.78; 62.67; 62.62; 62.53; 62.28; 62.20; 60.41; 55.01; 53.10; 48.25; 42.44; 40.90; 39.79; 37.70; 31.91; 29.69; 29.34; 26.70; 22.67; 14.04 (2×, Me); 14.01 (Me); 13.96 (Me); 13.87 (Me); 13.76 (Me); 13.73 (Me). FAB-MS: 1947.5 (100, M^+, $^{13}C^{12}C_{118}H_{70}O_{28}$; calc. 1947.4), 1902.2 (74, $[M-C_2H_5O]^+$), 1630.9 (6, $[M-C_{14}H_{20}O_8]^+$), 839.9 (20, $[C_{70}]^+$).

(±)-Hexadecaethyl Octakis(methano)[70]fullerene-71,71,72,72,73,73,74,74,75,75,76,76,77,77,78,78-hexadecacarboxylate (C_2-symmetrical, position of the methano addends on the fullerene surface unknown). *Product of* Fr. B-VI. Red-brown solid. R_f (CH_2Cl_2/AcOEt 95:5): 0.36. UV/VIS (CH_2Cl_2): 513 (5100), 484 (3600), 421 (sh, 3900), 387 (sh, 12200), 344 (sh, 23000), 276 (sh, 66000). IR (KBr): 2981*w*, 2933*w*, 1744*s*, 1633*w*, 1465*w*, 1445*w*, 1389*w*, 1367*w*, 1296*m*, 1235*s*, 1094*m*, 1022*m*, 858*w*, 729*w*, 668*w*, 637*w*, 584*w*, 568*w*, 513*w*, 500*w*, 456*w*, 447*w*, 404*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.65–4.05 (*m*, 32 H); 1.50–1.10 (*m*, 48 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 166.13 (C=O); 164.88 (C=O); 164.72 (C=O); 164.18 (C=O); 164.02 (C=O); 163.91 (C=O); 163.50 (C=O); 161.64 (C=O); 153.62; 152.22; 150.34; 149.40; 149.12; 148.53; 148.09; 147.74; 147.43; 145.72; 143.60; 141.57; 141.47; 141.38; 141.08; 141.04; 139.76; 138.46; 136.18; 136.01; 135.83; 135.79; 133.57; 133.33; 133.02; 132.99; 131.70; 70.15; 65.96; 63.36; 63.31; 63.24; 63.05; 62.91; 62.74; 62.67; 62.37; 62.09; 61.01; 58.15; 57.94; 56.66; 55.39; 54.22; 42.24; 41.95; 14.06 (Me); 14.01 (Me); 13.96 (Me); 13.85 (Me); 13.82 (Me); 13.78 (Me); 13.75 (Me); 13.72 (Me). FAB-MS: 2105.3 (100, M^+, $^{13}C^{12}C_{125}H_{80}O_{32}$; calc. 2105.5), 2060.2 (41, $[M-C_2H_5O]^+$), 1947.9 (43, $[M-C_7H_{10}O_4]^+$), 1788.7 (85, $[M-C_{14}H_{20}O_8]^+$), 839.9 (49, $[C_{70}]^+$).

Hexadecaethyl Octakis(methano)[70]fullerene-71,71,72,72,73,73,74,74,75,75,76,76,77,77,78,78-hexadecacarboxylate (C_1-symmetrical, position of the methano addends on the fullerene surface unknown). *Product of* Fr. B-VII. Black solid. R_f (CH_2Cl_2/AcOEt 95:5): 0.27. UV/VIS (CH_2Cl_2): 475 (1800), 442 (sh, 1200), 391 (sh, 9800), 374 (sh, 12400), 339 (sh, 29700), 282 (sh, 68100), 251 (96000). IR (KBr): 2978*w*, 2933*w*, 1744*s*, 1631*w*, 1575*w*, 1522*w*, 1464*w*, 1444*w*, 1389*w*, 1367w, 1297*m*, 1233*s*, 1166*w*, 1094*m*, 1019*m*, 858*w*, 758*w*, 722*w*, 686*w*, 581*w*, 502*w*, 455*w*, 402*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.65–4.05 (*m*, 32 H); 1.50–1.05 (*m*, 48 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 165.94 (C=O); 164.59 (C=O); 164.25 (C=O); 164.18 (C=O); 164.01 (C=O); 163.94 (C=O); 163.88 (C=O); 163.65 (C=O); 163.41 (C=O); 163.22 (C=O); 163.18 (C=O); 162.74 (C=O); 162.66 (C=O); 162.06 (C=O); 161.74 (C=O); 161.24 (C=O); 149.91; 148.25; 147.47; 146.39; 145.63; 145.39; 144.91; 144.82; 144.40; 144.14; 144.11; 143.66; 143.13; 142.86; 142.51; 141.58; 140.97; 140.86; 140.71; 140.28; 139.56; 139.33; 139.03; 139.00; 138.78; 138.68; 138.12; 138.09; 137.57; 137.50; 137.20; 136.11; 135.73; 135.41; 135.18; 135.15; 134.73; 133.91; 133.36; 132.31; 132.17; 131.42; 131.07; 130.64; 130.23; 130.11; 130.06; 129.61; 129.08; 128.79; 127.73; 127.10; 126.60; 126.47; 71.66; 71.60; 71.03; 66.88; 66.44; 65.41; 64.15; 63.63; 63.23; 63.07; 62.99; 62.91; 62.84; 62.74; 62.67; 62.57; 62.44; 62.41; 62.25; 62.11; 61.39; 58.45; 58.38; 55.05; 54.90; 54.08; 52.98; 52.55; 47.29; 46.00; 43.03; 41.66; 40.86; 40.13; 14.08 (Me); 14.03 (Me); 14.01 (Me); 13.96 (Me); 13.93 (Me); 13.91 (Me); 13.88 (Me); 13.83 (Me); 13.80 (Me); 13.78 (Me); 13.73 (Me); 13.49 (Me). FAB-MS: 2105.3 (100, M^+, $^{13}C^{12}C_{125}H_{80}O_{32}$; calc. 2105.5), 2060.3 (49, $[M-C_2H_5O]^+$), 1947.5 (12, $[M-C_7H_{10}O_4]^+$), 1788.8 (10, $[M-C_{14}H_{20}O_8]^+$), 839.9 (33, $[C_{70}]^+$).

Hexadecaethyl Octakis(methano)[70]fullerene-71,71,72,72,73,73,74,74,75,75,76,76,77,77,78,78-hexadecacarboxylate (C_1-symmetrical, position of the methano-addends on the fullerene surface unknown). *Product of* Fr. B-X. Black solid. R_f (CH_2Cl_2/AcOEt 95:5): 0.16. UV/VIS (CH_2Cl_2): 594 (144), 547 (sh, 2100), 513 (5100), 481 (4300), 421 (sh, 5800), 385 (sh, 11000), 354 (16100), 269 (sh, 39500). IR (KBr): 2980*w*, 2933*w*, 2906*w*, 2891*w*, 1743*s*, 1635*w*, 1465*w*, 1444*w*, 1389*w*, 1367*w*, 1296*m*, 1232*s*, 1175*w*, 1094*m*, 1024*m*, 858*w*, 811w, 772*w*, 756*w*, 728*w*, 707*w*, 668*w*, 637*w*, 584*w*, 562*w*, 512*w*, 478*w*, 456*w*, 410*w*, 408*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.60–4.05 (*m*, 32 H); 1.50–1.10 (*m*, 48 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 166.18 (C=O); 166.07 (C=O); 166.04 (C=O); 165.96 (C=O); 164.93 (C=O); 164.79 (C=O); 164.19 (C=O); 164.16 (C=O); 164.03 (C=O); 163.98 (C=O); 163.54 (C=O); 161.97 (C=O); 161.69 (C=O); 153.91; 153.41; 153.30; 152.39; 152.25; 150.51; 149.52; 149.49; 148.47; 148.42; 148.16; 147.77; 147.70; 147.45; 147.39; 147.14; 145.70; 145.35; 143.58; 143.43; 141.96; 141.52; 141.46; 141.43; 141.39; 141.20; 141.11; 141.08; 140.98; 140.75; 140.64; 139.59; 138.60; 138.56; 136.64; 136.32; 136.03; 135.88; 135.79; 135.69; 135.67; 134.15; 133.73; 133.37; 133.34; 133.19; 132.93; 132.61; 132.11; 131.88; 131.61; 70.26; 66.17; 66.03; 63.63; 63.60; 63.40; 63.25; 63.18; 63.06; 62.91; 62.76; 62.69; 62.39; 62.09; 62.03; 61.72; 61.65; 61.05; 58.36; 58.23; 57.97; 57.84; 56.64; 56.43; 56.04; 55.49; 55.37; 54.20; 54.08; 42.42; 42.31; 41.96; 41.63; 33.09; 14.10 (Me); 14.08 (Me); 14.04 (Me); 14.00 (Me); 13.88 (Me); 13.86 (Me); 13.85 (Me); 13.81 (Me); 13.77 (Me); 13.75 (Me). FAB-MS: 2106.1 (29, M^+, $^{13}C^{12}C_{125}H_{80}O_{32}$; calc. 2105.5), 2061.5 (9, $[M-C_2H_5O]^+$), 1948.4 (100, $[M-C_7H_{10}O_4]^+$), 1788.7 (35, $[M-C_{14}H_{20}O_8]^+$), 839.9 (36, $[C_{70}]^+$).

Conversion of **15** *to Higher C_{70} Adducts. i*) Application of the same reaction conditions (2 h) and the same workup as indicated above (synthesis of product *Fr. A-I – A-VI*) to the conversion of **15** (50 mg, 0.043 mmol), diethyl 2-bromomalonate (62 mg, 0.259 mmol), and DBU (40 mg, 0.259 mmol) in Me_2SO (20 ml) afforded seven C_{70} adduct fractions. *Fr. C-I:* bis-adduct **15** (starting material, 1 mg, 4%); *Fr. C-II:* tetrakis-adduct **17** (5 mg, 8%); *Fr. C-III:* pentakis-adduct(s) (2 mg, 3%); *Fr. C-IV:* hexakis-adduct(s) (4 mg, 5%); *Fr. C-V:* octakis-adduct (12 mg, 13%); *Fr. C-VI:* octakis-adduct(s) (6 mg, 6%); *Fr. C-VII:* octakis-adduct(s) (1 mg, 1%).

Octaethyl 1,2:31,32:41,58:65,66-Tetrakis(methano)[70]fullerene-71,71,72,72,73,73,74,74-octacarboxylate (**17**). *Product of* Fr. C-II. Black solid. R_f (CH_2Cl_2): 0.65. UV/VIS (CH_2Cl_2): 702 (1000), 646 (sh, 2500), 617 (5500), 569 (3800), 501 (11300), 444 (14400), 393 (sh, 15100), 362 (21300), 316 (sh, 31800), 289 (sh, 59700), 269 (sh, 85400), 257 (98100). IR (KBr): 2978*w*, 2931*w*, 2869*w*, 1744*s*, 1636*w*, 1579*w*, 1542*w*, 1463*w*, 1443*w*, 1403*m*, 1367*m*, 1294*m*, 1275*m*, 1252*s*, 1225*s*, 1183*m*, 1092*m*, 1055*w*, 1023*m*, 859*w*, 795*w*, 755*w*, 730*w*, 709*w*, 687*w*, 668*w*, 581*w*, 538w, 522*w*, 503*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.60–4.40 (*m*, 12 H); 4.20 (*q*, *J* = 7.0, 4 H); 1.47 (*t*, *J* = 7.1, 18 H); 1.22 (*t*, *J* = 7.3, 6 H); 1.20 (*t*, *J* = 7.1, 6 H). ^{13}C-NMR (100.6 MHz, $CDCl_3$, *ca.* 40 mM [$Cr(acac)_3$]): 164.26 (C=O); 163.39 (C=O); 163.36 (C=O); 153.52; 153.31; 148.53; 147.93; 147.23; 143.84; 142.96; 142.13; 141.77; 141.52; 141.00; 137.70; 136.39; 136.27; 132.72; 132.59; 124.04; 67.52 (fullerene sp^3-C); 66.43 (fullerene sp^3-C); 63.28; 63.08; 63.02; 62.39; 40.62 (methano bridge); 38.64 (methano bridge); 14.05 (Me); 14.00 (Me); 13.62 (Me). FAB-MS: 1472.9 (100, M^+, $^{13}C^{12}C_{97}H_{40}O_{16}$; calc. 1473.2), 1427.6 (12, $[M - C_2H_4O]^+$), 840.0 (34, $[C_{70}]^+$).

(±)-Hexadecaethyl Octakis(methano)[70]fullerene-71,71,72,72,73,73,74,74,75,75,76,76,77,77,78,78-hexadecacarboxylate (C_2-symmetrical, position of the methano-addends on the fullerene surface unknown). *Product of* Fr. C-V. Green solid. R_f (CH_2Cl_2/AcOEt 98.5:1.5): 0.30. UV/VIS (CH_2Cl_2): 695 (700), 677 (sh, 1000), 636 (2200), 589 (2100), 490 (3800), 419 (sh, 6900), 289 (sh, 41800), 271 (sh, 48600). IR (KBr): 2958*w*, 2922*w*, 2853*w*, 1744*s*, 1711*m*, 1668*m*, 1653*w*, 1464*w*, 1447*w*, 1388*w*, 1367w, 1294*m*, 1253*s*, 1222*s*, 1175*m*, 1093*m*, 1024*m*, 858*w*, 806*w*, 750*w*, 739*w*, 715*w*, 698*w*, 667*w*, 579*w*, 559*w*, 544*w*, 481*w*, 452*w*, 418*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.55–4.10 (*m*, 32 H); 1.50–1.15 (*m*, 48 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 164.66 (C=O); 164.58 (C=O); 164.37 (C=O); 163.98 (C=O); 163.63 (C=O); 163.18 (C=O); 162.71 (C=O); 162.60 (C=O); 148.18; 144.66; 144.41; 144.16; 143.03; 142.41; 141.65; 141.50; 140.64; 140.40; 139.04; 137.06; 136.72; 136.08 (2×); 135.84; 135.11; 135.05 (2 x); 134.69; 133.69; 133.37; 131.42; 131.40; 128.67; 127.02; 124.85; 75.13; 72.07; 69.51; 63.78; 63.62; 63.41; 62.70; 62.61; 62.50; 62.15; 62.08; 62.04; 58.61; 58.58; 54.81; 43.95; 42.05; 41.47; 41.27; 33.78; 13.98 (Me); 13.88 (Me); 13.79 (Me); 13.75 (Me); 13.66 (Me). FAB-MS: 2105.7 (100, M^+, $^{13}C^{12}C_{125}H_{80}O_{32}$; calc. 2105.5), 2060.6 (46, $[M - C_2H_5O]^+$), 1947.4 (27, $[M - C_7H_{10}O_4]^+$), 1789.3 (28, $[M - C_{14}H_{20}O_8]^+$), 840.0 (50 $[C_{70}]^+$).

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