125. Multiple Cyclopropanations of C_{70}

Synthesis and Characterization of Bis-, Tris-, and Tetrakis-adducts and Chiroptical Properties of Bis-adducts with Chiral Addends, Including a Recommendation for the Configurational Description of Fullerene Derivatives with a Chiral Addition Pattern

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(31.VII.95)

The regioselectivity of multiple cyclopropanations of C_{70} with 2-bromopropanedioates in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as base (*Bingel* reaction) was investigated in a systematic study. Bis-adduct formation occurred preferentially at the 6–6 bonds formed by the most pyramidalized sp^2-C-atoms at the two opposite poles of the fullerene and, in the reaction with achiral bis[(ethoxycarbonyl)methyl] 2-bromopropanedioate (**13a**), yielded three constitutionally isomeric bis(methano)fullerenes (*Scheme 2*). Two of them, C_2-symmetrical (±)-**1** and (±)-**2**, are chiral; a fact which had not been considered in previous investigations. Formation of the third, C_{2v}-symmetrical isomer **3** was observed for the first time. Configurational descriptions for fullerene derivatives which possess a chiral chromophore as a result of specific functionalization patterns are proposed. Cyclopropanations of C_{70} with optically active bis[(*S*)-1-phenylbutyl] 2-bromopropanedioate (**13b**) yielded five optically active, C_2-symmetrical bis-adducts **7**–**11** which could be separated by preparative HPLC and fully characterized (*Scheme 3*, *Fig. 4*). Compounds **7**/**8** and **9**/**10** represent two constitutionally isomeric pairs of diastereoisomers, and their circular dichroism (CD) spectra show pronounced *Cotton* effects mainly due to strong chiroptical contributions from the chirally functionalized fullerene chromophores (*Fig. 7*). Since the addition patterns on the fullerene surface in each pair of diastereoisomers have an enantiomeric relationship, their CD spectra closely resemble those expected for two enantiomers. In the third constitutional isomer **11**, the addition pattern on the fullerene surface is C_{2v}-symmetrical, and optical activity only results from the chiral addends. Its CD spectrum shows weak *Cotton* effects mainly from induced circular dichroism originating from the perturbation of the achiral fullerene chromophore by the attached chiral addends. Addition of diethyl 2-bromopropanedioate (2 equiv.) to the C_2-symmetrical racemic bis-adduct (±)-**2** yielded a mixture of tris-adducts and one major, C_2-symmetrical tetrakis-adduct (±)-**4** which was isolated in pure form (*Scheme 4*). Starting from the achiral C_{2v}-symmetrical bis-adduct **3**, one single C_s-symmetrical tris-(**5**) and one C_{2v}-symmetrical tetrakis-adduct (**6**) were obtained as major products which were isolated and fully characterized (*Scheme 5*). The regioselectivity for introduction of a second addend in the same hemisphere of C_{70} is high and resembles the preferred pattern of bis-addition seen in the functionalization of C_{60}.

1. Introduction. – Regioselective formation of fullerene multiple adducts [1] [2] provides the opportunity for studying the changes in chemical reactivity and physical properties which occur when the conjugated fullerene chromophore is reduced as a result of increasing functionalization [3]. In addition, the development of selective methods for multiple-adduct formation provides access to an unprecedented variety of three-dimensional building blocks for organic chemistry, which nicely complement the present repertoire of two-dimensional acetylenic, olefinic, and benzenoid components for the construction of tailor-made functional molecules and polymers.

A great variety of multiple adducts have been reported for buckminsterfullerene C_{60} [4–9], and the principles governing the regioselectivity seen in particular in the formation

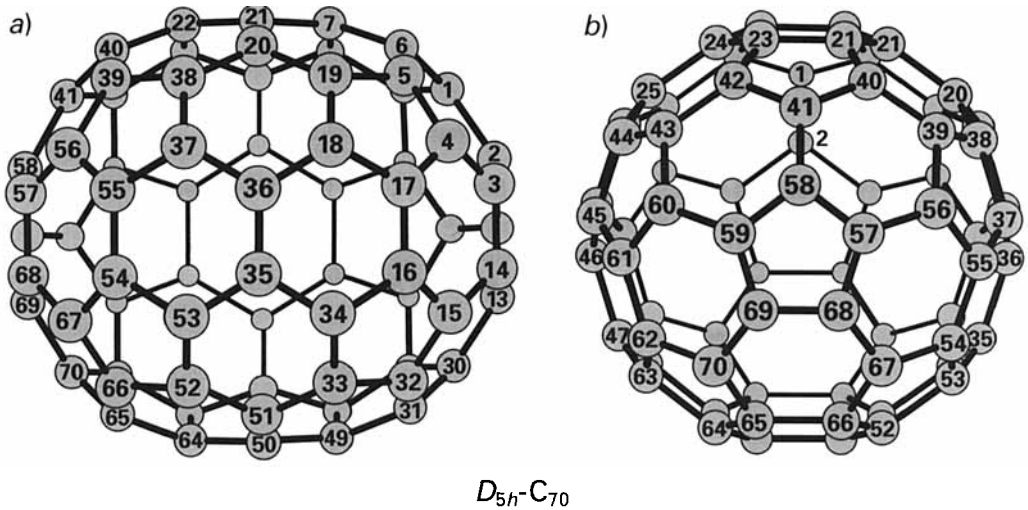


Fig. 1. *Views on* D_{5h}-C_{70} a) *perpendicular to and* b) *along the* C_5-*symmetry axis.* The numbering of C-atoms was done according to [11a] and differs from the one previously utilized [11b] [12e] [13].

of higher adducts by this most abundant fullerene are becoming increasingly transparent [7] [9]. Much less is known about multiple additions to the higher fullerene C_{70} (*Fig. 1*) which is the topic of the present investigation. Not only is this C-allotrope less abundant than C_{60}, but its covalent chemistry is complicated by the fact that, in contrast to C_{60} with only two different types of bonds, there are eight distinct bonds at which mono-functionalization may occur. Four of the bonds in C_{70} are located at the junction between two six-membered rings (6–6 bonds, $\alpha-\kappa$ type, shown in the *Schlegel* diagram of *Fig. 2, a*) and another four at the junction between a six- and a five-membered ring (6–5 bonds). Therefore, to prevent formation of overly complex product mixtures, a project aimed at exploring multiple functionalizations of C_{70} preferentially utilizes a reaction that minimizes the number of isomers formed during the first addition step.

A reaction that fulfills this requirement is the *Bingel* reaction, the nucleophilic cyclopropanation with 2-bromomalonates in the presence of base yielding methanofullerene structures with a closed transannular bond at the 6-6 ring junction (6-6 closed) [10]. When applied to C_{70}, the *Bingel* reaction generates with high regioselectivity the product from attack at the C(1)–C(2) bond (an α-type bond, *Fig. 2, a* and *b*) [11] close to the pole of the fullerene, where the pyramidalization of the sp^2-C-atoms is highest[1]). In C_{70}, pyramidalization of sp^2-C-atoms and C–C bond curvature decrease when passing from the poles to the equator. Hence, the fullerene undergoes preferential mono-attack at the α-type and, to a lesser extent, the β-type bonds close to the poles (*Fig. 2, a*), since addition to these bonds is accompanied by the highest release of strain resulting from the pyramidalization of sp^2-C-atoms. Mono-adducts from attack at α- and β-type bonds

[1]) In this paper, the new C-atom numbering for C_{70} proposed by *Taylor* and recommended to IUPAC is used [11a]. It differs from the numbering used in previous studies [11b] [12e] [13].

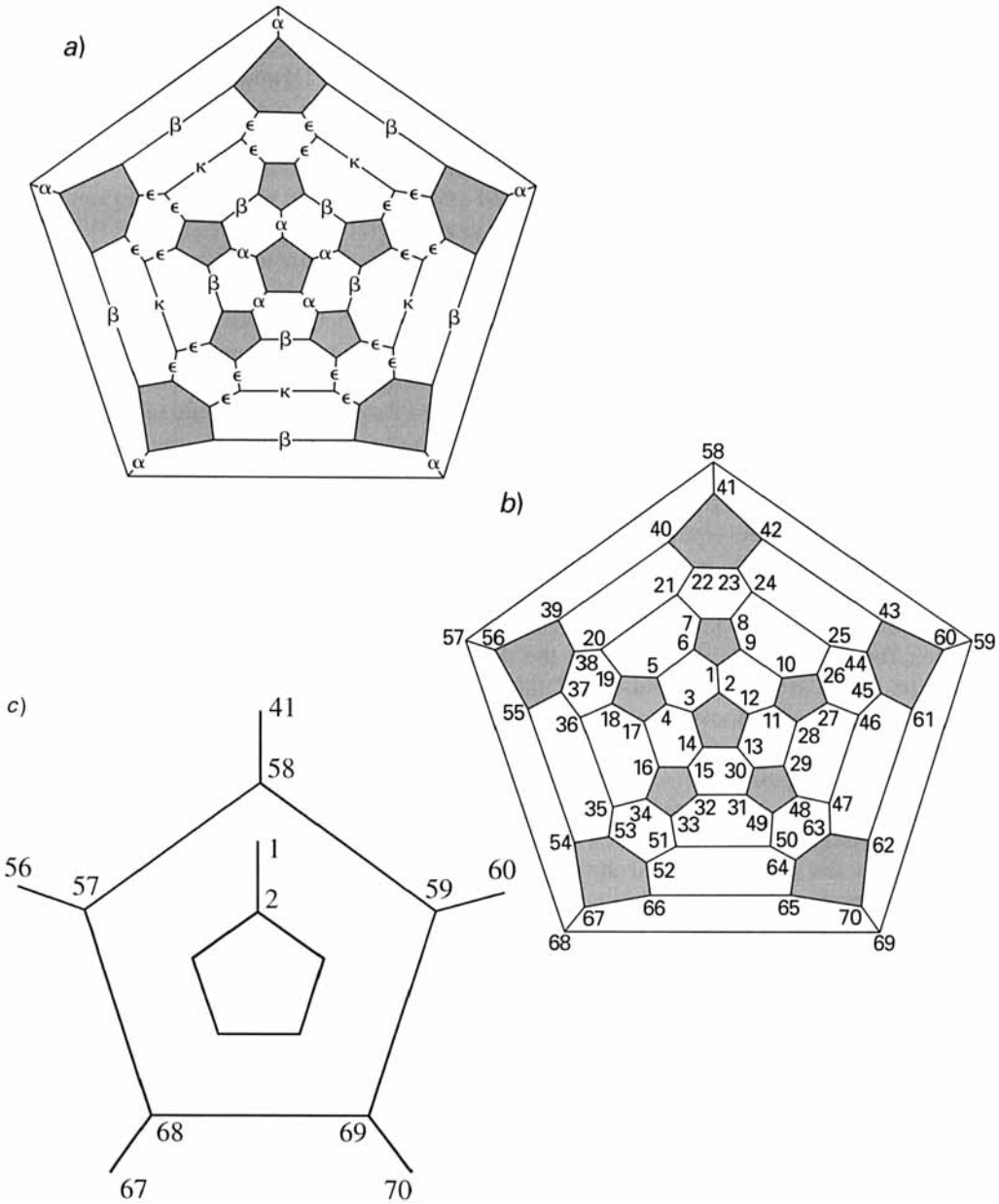


Fig. 2. Schlegel *diagrams* [12e] *showing* a) *the four different types* α–κ *of* 6–6 *bonds and* b) *the numbering of the C-atoms in* C_{70}. c) Newman-*type projection showing the five possible sites for bis-addition to* α-*bonds at the unfunctionalized pole of a* C_{70} *derivative bearing an addend at the C(1)–C(2)* α-*type bond.* In the projection of *Fig. 2, c*, 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 five α-type bonds adjacent to the distal pentagon, which are the sites of bis-addition, are pointing outside.

were reported for transition-metal complexations [12a], osmylations [12b], nucleophilic hydro-alkylations and -arylations [12c], hydrogenations [12d], *Diels-Alder* cycloadditions [12e, f], and [3+2] dipolar cycloadditions with nitrile oxides [12g] and with diazomethane followed by photochemical N_2 extrusion [12h]. Today, only one mono-addition to one of the less curved ε-type bonds has been reported [12e], whereas mono-adducts from 1,2-addition to the κ-type bonds close to the equator remain unknown [12i].

Two X-ray crystal structures of *Diels-Alder* adducts at the C(1)–C(2) (α-type) and the C(5)–C(6) (β-type) bonds provided useful guidance for the present study [13]. The analysis of these structures showed that the bonds at the unfunctionalized pole in both adducts have about the same length and curvature as the corresponding bonds in free C_{70}. This in return suggested that the bonds at the unfunctionalized pole would have similar reactivity to those in free C_{70}, and that bis-adduct formation would preferentially occur at the reactive 6–6 bonds of the second pole rather than at the pole that is already functionalized. Therefore, we expected that a second *Bingel* reaction would take place at the hitherto unfunctionalized pole and, similarly to the initial mono-cyclopropanation, would yield products from attack at the five α-type bonds C(41)–C(58), C(56)–C(57), C(59)–C(60), C(67)–C(68), and C(69)–C(70) (*Fig. 2, b* and *c*). These bonds are shown in *Fig. 2, c*, in a *Newman*-type projection along the C_5 axis passing through the middle of the two polar pentagons of both C_{70} hemispheres. In this projection, the inner five-membered ring represents the proximal polar pentagon, and the attached vertical line depicts the functionalized α-type bond (C(1)–C(2)) where the first addition occurred. The larger outer five-membered ring represents the distal polar pentagon, and the five adjacent α-type bonds are pointing outside. If the malonate addend is achiral, bis-addition to α-type bonds on opposite poles yields three constitutionally isomeric bis(methano)-fullerenes, one achiral (C_{2v}-symmetrical) and two chiral ones (C_2-symmetrical) which each are formed as pairs of enantiomers. This is nicely illustrated by the *Newman*-type projection in *Fig. 2, c*: a second cyclopropanation at C(56)–C(57) and C(59)–C(60) or C(67)–C(68) and C(69)–C(70), respectively, leads to the formation of racemic mixtures.

Only a few papers reported the selective formation of multiple adducts of C_{70} [11a] [14]. In agreement with the expectations derived from the X-ray structural analysis, all bis-1,2-additions occurred at opposite poles of the fullerene [14a, b]. *Zhang* and *Foote* reported the formation of bis-adducts by [2+2] cycloaddition of *N,N,N′,N′*-tetraethylethyne-1,2-diamine to two α-type bonds on opposite poles of C_{70}. They found that the five α-bonds at the unfunctionalized pole of the mono-adduct showed significantly different reactivity towards the second addend. The C_2-symmetrical racemic 1,2:56,57- and 1,2:67,68-adducts were obtained in a 9:1 ratio and characterized as a product mixture [14b]. The formation of the third possible constitutional isomer resulting from addition at the C(1)–C(2) and C(41)–C(58) bonds was not observed. With the exception of $C_{70}Cl_{10}$, formed by radical addition [11a], and $C_{70}H_4$ [14c], defined higher adducts of C_{70} have so far not been reported.

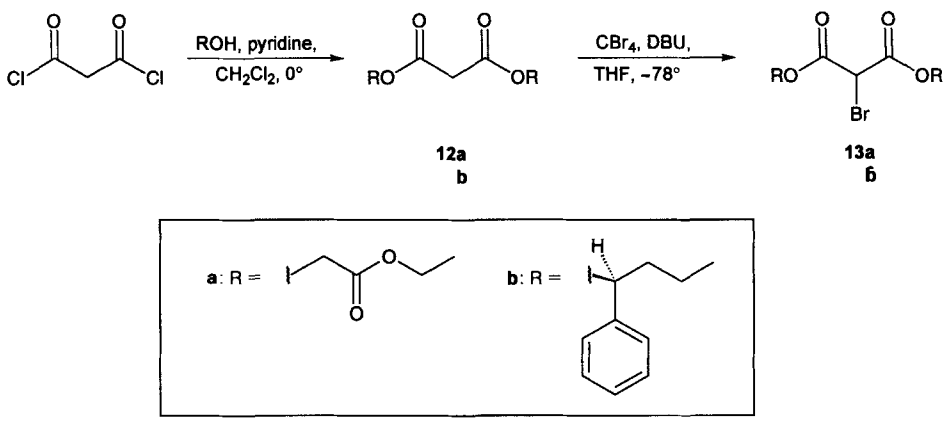
Here we present isolation and characterization of all three constitutional isomers (±)-**1**, (±)-**2**, and **3** formed by double *Bingel* addition to α-type bonds at the two opposite poles of C_{70} and, starting from bis-adducts (±)-**2** and **3**, the regioselective formation of tris- (**5**) and tetrakis-adducts (±)-**4** and **6**. In order to isolate all five possible bis-adducts derived from attack at two α-type bonds on opposite poles, *Bingel* additions with chiral 2-bromomalonates were performed. These reactions led to two constitutionally isomeric

pairs of optically active diastereoisomers, **7**/**8** and **9**/**10**, in addition to a third constitutional, optically active isomer **11**, which could all be separated and isolated in pure state. Configurational descriptions for fullerene adducts which possess a chiral chromophore as a result of specific functionalization patterns are proposed.

Fullerene chirality, which is at the center of much of the work described below, can be expressed in several ways. Some higher fullerenes, such as D_2-C_{76}, D_3-C_{78}, or D_2-C_{84} as well as their covalent derivatives are inherently chiral molecules [12e] [15]. A second class of chiral derivatives form upon functionalization of achiral fullerenes such as C_{60} or C_{70} with chiral addends such as sugar derivatives [16a–c], peptides [16d–f], or others [16g]. Finally, a third class of derivatives of achiral fullerenes becomes chiral as a result of a distinct functionalization pattern. Known examples are three chiral C_2-symmetrical bis-adducts and a C_3-symmetrical as well as a D_3-symmetrical tris-adduct of C_{60} [7] [17]. Also, C_{70} derivatives formed by mono-addition to an ε-type bond are chiral [12e]. The occurrence of addition-pattern-mediated chirality in multiple adducts of C_{70} was not considered prior to this work.

2. Results and Discussion. – 2.1. *C_{70} Bis-adducts with Achiral Malonate Addends.* To investigate the regioselectivity of the bis-cyclopropanation of C_{70} in the *Bingel* reaction, a bulky and highly polar achiral, C_{2v}-symmetrical malonate addend was desirable. Bulkiness was expected to help directing the second addition to the unfunctionalized pole, and high polarity should facilitate separation of the bis-adducts from mono- and tris-adducts as well as the separation of the expected constitutionally isomeric bis-cyclopropanated products. Previous investigations on the formation of isomeric C_{60} pentakis-adducts had

Scheme 1. *Synthesis of Achiral* (**13a**) *and Chiral* (**13b**) *2-Bromomalonic Esters*



shown that bis[(ethoxycarbonyl)methyl] malonate addends significantly facilitate the chromatographic separation of constitutional isomers, as compared to simple diethyl malonate addends [9b] and, therefore, bis[(ethoxycarbonyl)methyl] 2-bromomalonate (**13a**), prepared by bromination of the corresponding malonate **12a** (*Scheme 1*), was chosen as the reagent.

Reaction of C_{70} with 1 equiv. of tetraester **13a** and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) yielded *ca.* 47% of the C_s-symmetrical mono-adduct **14** which was readily separated by chromatography (SiO_2, CH_2Cl_2) from the formed 10% bis-adducts (*Scheme 2*). The fullerene region of the ^{13}C-NMR spectrum of **14** showed all 35 distinct resonances expected for the fullerene sp^2-C-atoms. In agreement with the previous results by *Bingel* [10], preference for attack at the α-type bond was very high; only trace amounts of other mono-adducts were formed which could not be isolated.

Reaction of 1 equiv. of **13a** with purified **14** gave a mixture of bis-adducts in 75% yield. Addition of 2 equiv. of tetraester **13a** and DBU to a solution of C_{70} in toluene afforded mainly bis-adducts (69%) besides small quantities of mono-adduct (*Scheme 2*). The separation of the mono- from bis-adduct fractions was achieved in one run by gradient column chromatography (SiO_2, $CH_2Cl_2 \rightarrow CH_2Cl_2$/AcOEt 98.5:1.5). The bis-adducts were separated on silica gel *H* with CH_2Cl_2. Three fractions were obtained in a weight ratio of 1:6.2:2.8, suggesting the formation of three constitutional isomers. To tentatively assign structures (±)-**1**, (±)-**2**, and **3** to these isomers, we considered the elution order on the chromatographic phase [1] [7] [17]. The more polar the bis-adduct, the higher its retention time on a polar stationary phase should be. The C_{2v}-symmetrical isomer **3** is the most polar derivative with the highest molecular dipole moment, hence it was expected to elute last. With the C_2-symmetrical bis-adduct (±)-**1** being the least polar isomer, the chromatographic elution sequence suggested to assign the structures (±)-**1**, (±)-**2**, and **3** to the three fractions isolated in the weight ratio 1:6.2:2.8 shown above. This ratio differs substantially from a statistical product distribution of 2:2:1 for the three constitutional isomers. This shows that the two α-type bonds C(56)–C(57) and C(59)–C(60) (*Fig. 2*) that are attacked during the second cyclopropanation under formation of (±)-**2** are particularly activated by the first addend in mono-adduct **14**. Presumably, a combination of steric and electronic factors, such as the magnitude of the coefficients of the *l*owest *u*noccupied *m*olecular *o*rbital (LUMO), to which the electron density of the incoming nucleophile is transferred, are responsible for the observed kinetic preference for bis-addition leading to (±)-**2**. Based on similar steric and electronic considerations, *Hirsch* and coworkers had previously explained the regioselectivity seen in multiple *Bingel* cyclopropanations of C_{60} [7b]. The ratio of (±)-**1** to (±)-**2** (1:6.2) corresponds to the one (1:9) previously reported by *Zhang* and *Foote* for bis-adducts with fullerene functionalization patterns identical to those in (±)-**1** and (±)-**2**, which are formed by twofold [2+2] cycloaddition of *N,N,N'N'*-tetraethylethyne-1,2-diamine to C_{70} [14b].

Firm confirmation of the assignments based on the chromatographic elution order was obtained by the NMR-spectral characterization of the three constitutionally isomeric bis-adducts. In agreement with the assigned C_2-symmetry[2]) of (±)-**1** and (±)-**2**, their ^{13}C-NMR spectra show 33 distinct peaks in the typical fullerene spectral region (between 130 and 160 ppm). In addition, two signals around 67 ppm for the bridgehead sp^3-C-atoms are visible. The ^{13}C-NMR spectrum of the third isomer (**3**) shows only 19 lines in the fullerene spectral region and two signals for the bridgehead sp^3-C-atoms. Five of the resonances in the fullerene region display half intensities and originate from the sp^2-C-

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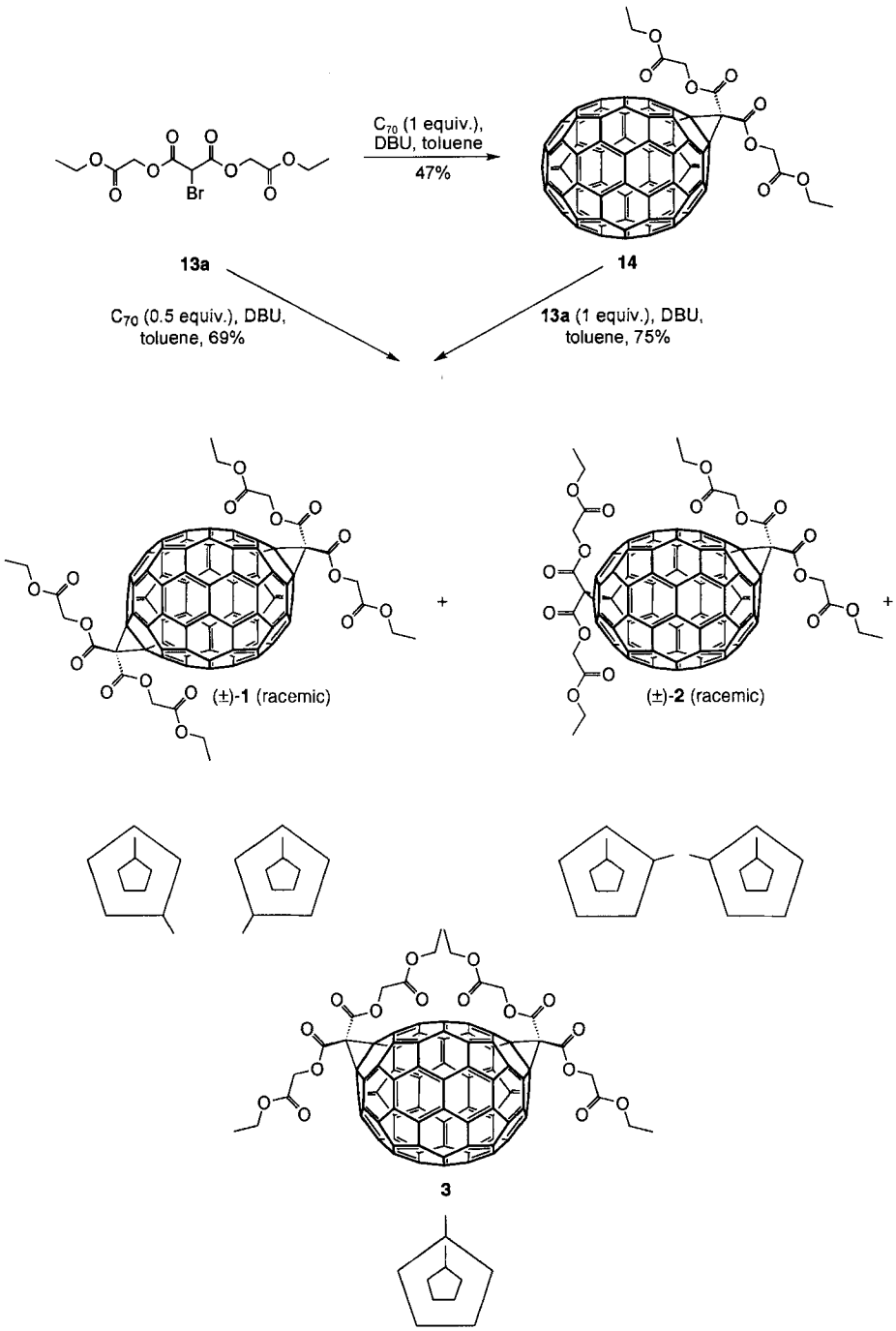
[2]) The C_2-symmetry axis passes through the middle of one of the five equatorial bonds at one side and the center of one of the equatorial six-membered rings at the other side of the molecule.

Scheme 2. *Synthesis of C_{70} Mono-adduct* **14** *and Isomeric Bis-adducts (±)-***1**, *(±)-***2**, *and* **3**. *Newman*-type projections (see *Fig. 2*) for the bis-adducts are shown.



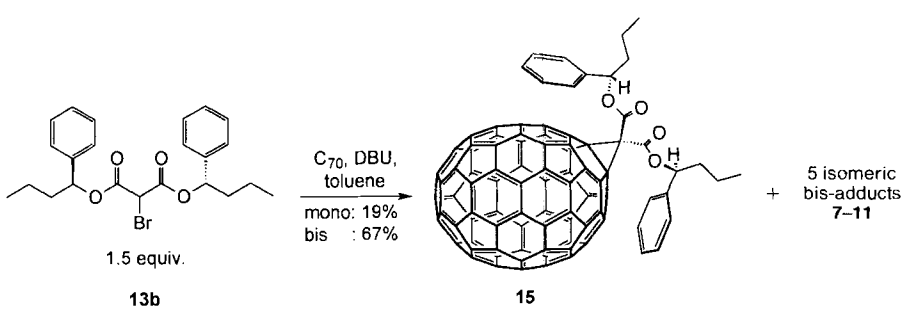
atoms on the equator of the fullerene. These results support the C_{2v}-symmetrical structure assigned to **3**, which provides the first example for this bis-functionalization pattern. If the second additions had occurred at β-type bonds at the unfunctionalized pole of **14**, four C_1- and one C_s-symmetrical bis-adducts would have formed with ^{1}H- and ^{13}C-NMR spectra distinctively different from those recorded.

The UV/VIS spectra of mono-adduct **14** and the three bis-adducts (±)-**1**, (±)-**2**, and **3** show the onset of absorption between 700 and 720 nm and a pronounced maximum around 460 nm. The C_{2v}-symmetrical bis-adduct **3** shows a characteristic absorption maximum at λ_{max} 270 nm, which is neither observed in mono-adduct **14** nor in the other, C_2-symmetrical bis-adducts.

2.2. *Optically Active C_{70} Bis-adducts with Chiral Malonate Addends.* Bis-functionalization of C_{70} with achiral C_{2v}-symmetrical malonate addends occurred at the five α-type bonds at the unfunctionalized pole of mono-adduct **14** and generated five isomers, two constitutionally isomeric pairs of C_2-symmetrical enantiomers and a third achiral, C_{2v}-symmetrical constitutional isomer. In analogy, the bis-addition with optically active, C_2-symmetrical malonate addends should yield five optically active isomers, two constitutionally isomeric pairs of C_2-symmetrical diastereoisomers as well as a third constitutional, C_2-symmetrical isomer. The latter would form by bis-cyclopropanation at the C(41)–C(58) bond (*Fig. 2, c*), and its chirality would only be determined by the chiral addend, since the addition pattern to the fullerene is C_{2v}-symmetrical. In contrast, second attack at the C(56)–C(57) and C(59)–C(60) bonds, and similarly at the C(67)–C(68) and C(69)–C(70) bonds, would produce the two pairs of diastereoisomers, in which the chirality of the C_2-symmetrical fullerene functionalization pattern adds to the chirality of the addends. All five isomers should be separable by chromatography on an achiral stationary phase.

As chiral reagent producing a C_2-symmetrical addend, we chose optically active bis[(*S*)-1-phenylbutyl] 2-bromomalonate (**13b**), which was prepared by esterification of malonyl dichloride with commercially available (*S*)-1-phenylbutanol to give **12b**, followed by bromination (*Scheme 1*). Computer and CPK molecular-model examinations had suggested that the Ph and butyl groups of the attached addend would generate sufficiently large shape differences in the five expected bis-adducts to allow their chromatographic separation.

Scheme 3. *Synthesis of the Optically Active C_{70} Mono-adduct* **15** *and Isomeric Bis-adducts* **7**–**11**



A solution of C_{70} in toluene was reacted with 1.5 equiv. of **13b** and DBU (*Scheme 3*) after which column chromatography (SiO_2, hexane/CH_2Cl_2 2:1) afforded mono-adduct (19%) besides a mixture of bis-adducts (67%) and a small amount of, probably, higher adducts. Pure mono-adduct **15** shows a ^{13}C-NMR spectrum containing 75 out of the 76 lines (68 fullerene core and 8 Ph resonances) expected in the fullerene and aromatic region (110–160 ppm) for a C_1-symmetrical derivative. To separate the isomeric bis-adducts, several stationary phases and solvent compositions were tested by anal. HPLC. The ultimate separation of the bis-adducts was achieved by prep. HPLC on a silica-gel column using a mixture of hexane/toluene 65:35 (*Fig. 3*). Five fractions (I–V) were collected, and fractions I and II were re-injected under the same conditions for complete separation. The five pure isomers from fractions I–V were obtained in a weight ratio of 1.4:1:9.3:8.8:4.8.

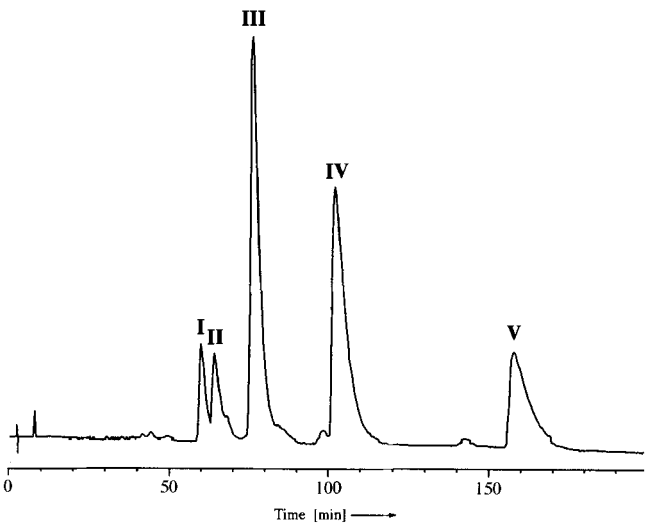


Fig. 3. *Prep. HPLC separation of the optically active C_{70} bis-adducts* **7**–**11**. Fractions I and II contain the pair of diastereoisomers **7**/**8**, fractions III and IV the pair of diastereoisomers **9**/**10**, and fraction V isomer **11**. Conditions: *Nucleosil 100-7* (*Macherey-Nagel*), hexane/toluene 65:35, flow rate 30 ml/min, detection at λ 310 nm.

The structures of the five expected C_2-symmetrical bis-adducts **7**–**11** are shown in *Fig. 4* together with the *Newman*-type projections introduced in *Sect. 2.1* which illustrate the isomeric relationships between the five compounds. In these projections, the star reflects 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 (inner) pentagon and on the left side (due to rotation around the C_2 axis) of the distal (outer) pentagon refers to the (*S*,*S*)-configuration of the addend. The depiction of the (*R*,*R*)-configuration would be just the other way around. According to the proposed configurational description for fullerene derivatives with chiral functionalization patterns (see *Insert*) the absolute configuration of the fullerene chromophore in the four bis-adducts **7**–**10** is specified as (^{r}*C*)-**7**, (^{r}*A*)-**8**, (^{r}*A*)-**9**, and (^{r}*C*)-**10**.

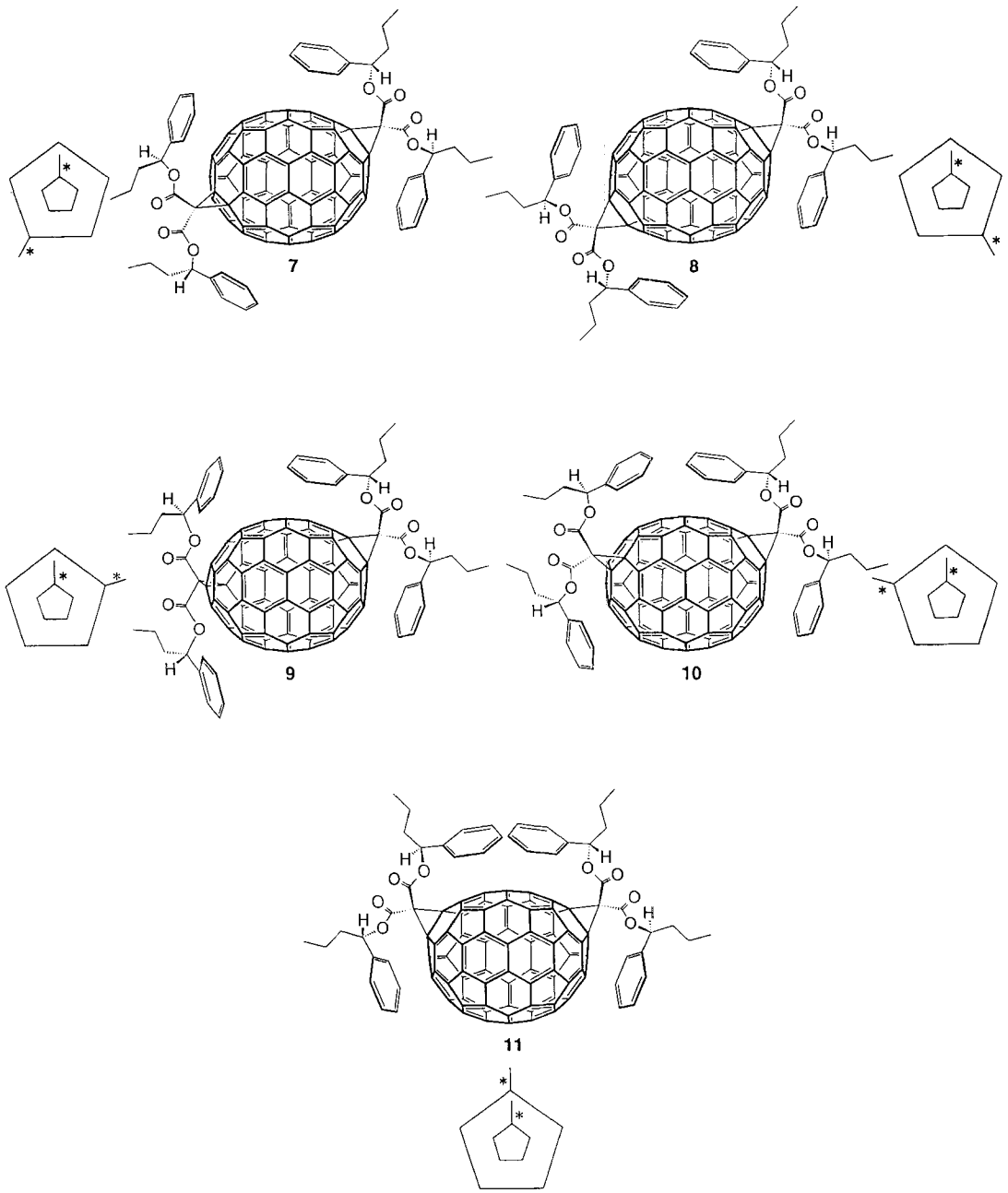
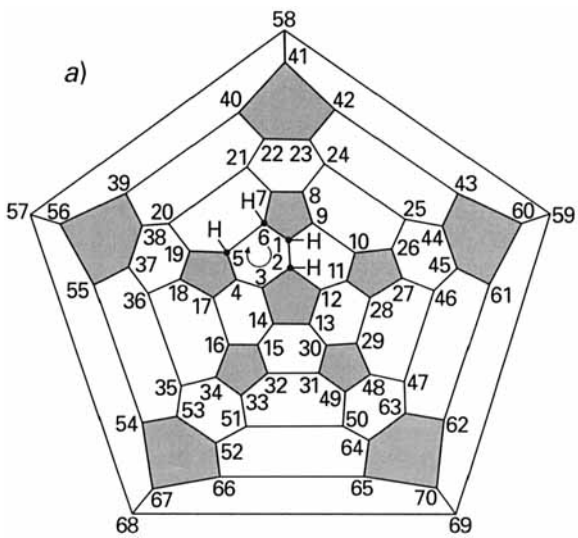


Fig. 4. *Structures of the five separated and characterized isomeric C_{70} bis-adducts* **7**–**11**. A *Newman*-type projection is shown for each isomer (see *Fig. 2*). The star reflects the presence of stereogenic centers with specified absolute configuration in the addends. The arbitrarily chosen orientation of the star on the right site of the proximal (inner) pentagon and on the left side (due to rotation around the C_2 axis) of the distal (outer) pentagon refers to the (*S*,*S*)-configuration of the addend. The depiction of the (*R*,*R*)-configuration would be just the other way around.

Recommendation for the Configurational Description of Fullerene Derivatives with a Chiral Addition Pattern

The configuration of fullerene adducts with a chiral addition pattern[1]) could in principle be described by indicating the configuration of each stereogenic center of the C-sphere. This procedure, however, seems of little use, mainly because the determination of the substituent priorities according to *Cahn*, *Ingold*, and *Prelog* (*CIP*) may be complicated by the multiple branching of the fullerene C-framework and the possible need to consider high generations of connected atoms before a difference in priority becomes apparent. Furthermore, if chiral derivatives with a large number of addends are considered, the procedure has to be repeated many times, and a name with a multitude of configurational descriptors results.

For these reasons, a simple convention for the description of the absolute configuration of fullerene adducts with a chiral addition pattern is recommended. It is based on the consideration that the numbering schemes proposed for fullerenes [1] are chiral themselves: in a three-dimensional model, the pathway following the sequence of numbered C-atoms is made up of a helix or of helical segments. It ensues that two enantiomeric numbering schemes are applicable to an inherently achiral fullerene.



a) *(*^{r}C*)-1,2,5,6-Tetrahydro[70]fullerene* [3]. The enantiomeric numbering scheme would lead to the name (*r*-*A*)-1,2,9,10-tetrahydro[70]fullerene which is wrong, because the locant set 1,2,5,6 is lower than 1,2,9,10.

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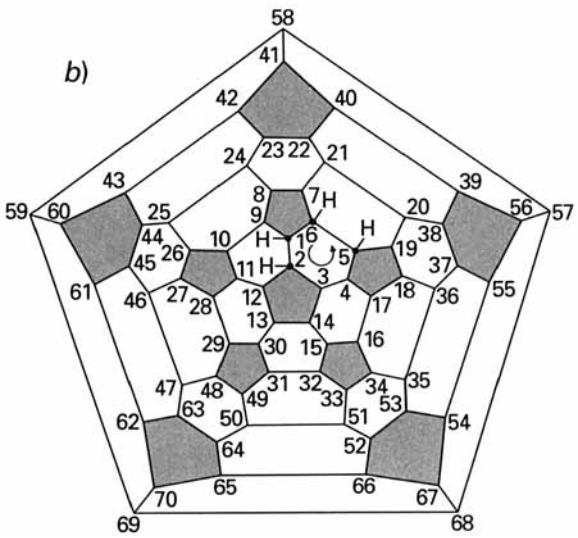
[1]) Possible stereogenic elements in the addends are described as usual; they are not discussed here.

For a chiral derivative resulting from a specific addition pattern of an inherently achiral fullerene, however, there is a unique numbering scheme that follows the basic nomenclature rule of the lowest set of locants for the addends [2]. Therefore, a characterization of the handedness of the numbering scheme leading to the lowest set of locants is sufficient to unambiguously describe the absolute configuration of the adduct.

The configurational description of the adduct is defined identical to that of the numbering scheme affording the lowest set of locants and can be determined in a simple way by using a three-dimensional representation, or more easily, a *Schlegel* diagram[2]) of the derivative. After determining the required numbering scheme, the viewer, facing the polygon of the numbering commencement, traces a path from C(1) to C(2) to C(3). If the path describes a *c*lockwise motion, the configuration of the adduct is termed ^{f}C, if it describes an *a*nti-clockwise motion, the descriptor is ^{f}A (the use of ^{f}A and ^{f}C [1a] for the configurational description of *f*ullerenes and their derivatives should prevent confusion with the descriptors *R* and *S* as used within the *CIP* system).

In practice, we suggest the following procedure: mirror images of the numbering scheme [1] fitting a *Schlegel* diagram of the fullerene in question are copied on a



b) (*f*A)*-1,2,5,6-Tetrahydro[70]fullerene*. The name of the enantiomer is identical with the exception of the stereochemical descriptor.

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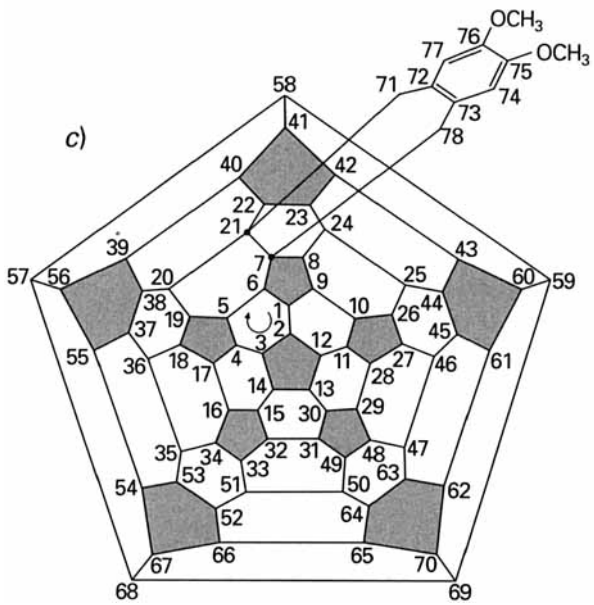
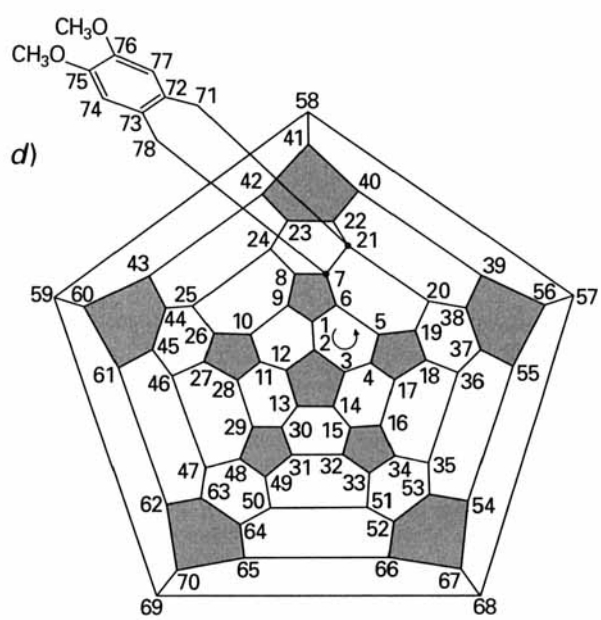
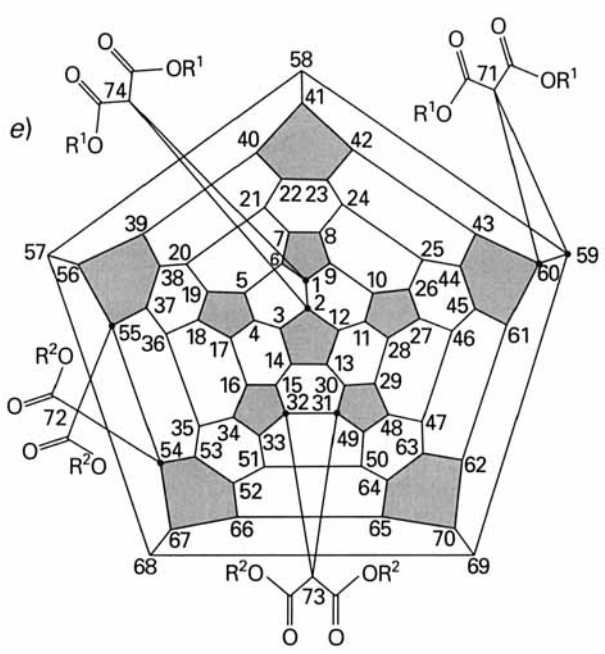
[2]) The convention that the central polygon of the *Schlegel* diagram is facing the viewer [1a] is used here.



c) *(ᶠC)-75,76-Dimethoxy-7,21-(methano[1,2]benzenomethano)[70]fullerene* [4]. An alternative name (ᶠ*A*)-75,76-dimethoxy-8,24-(methano[1,2]benzenomethano)[70]fullerene is wrong, because the locant set 7,21 is lower than 8,24.



d) *(ᶠA)-75,76-Dimethoxy-7,21-(methano[1,2]benzenomethano)[70]fullerene.*

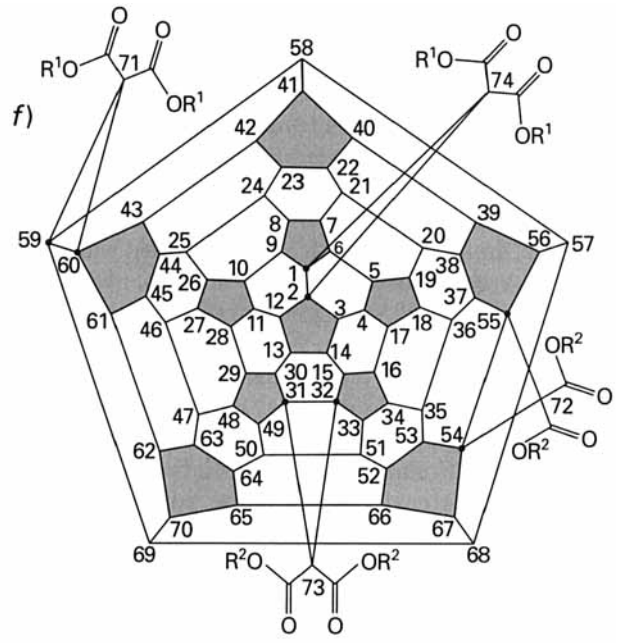


$R^1 = CH_2COOCH_2CH_3$
$R^2 = CH_2CH_3$

e) *71,71,74,74-Tetrakis[(ethoxycarbonyl)methyl] 72,72,73,73-Tetraethyl* (*f*C)*-1,2:31,32:54,55:59,60-Tetrakis(methano)[70]fullerene-71,71,72,72,73,73,74,74-octacarboxylate* (one enantiomer of **4** reported in this paper). An alternative name 72,72,74,74-tetrakis[(ethoxycarbonyl)methyl] 71,71,73,73-tetraethyl (*fA*)-1,2:31,32:56,57:61,62-tetrakis(methano)[70]fullerene-71,71,72,72,73,73,74,74-octacarboxylate is wrong, because the locant at the first point of difference is lower in the set of the former compared to that of the latter name (54 < 56).

transparency and, according to the recommendation given above, are assigned the descriptors *fA* and *fC*, respectively. These templates can be easily rotated in any required orientation and used to determine which one of the two allows for the lowest set of locants in a *Schlegel*-type representation of the chiral fullerene derivative. The absolute configuration of the adduct is assigned the descriptor of the numbering scheme fulfilling this criterion.

N.B. Care has to be taken upon transposition of a three-dimensional representation of a fullerene adduct into a *Schlegel* diagram. If there is a choice, the viewer has to face that side of the sphere where addends are located closest to the axis relevant for the numbering commencement [1a]. In case of C_{70}, this is the C_5 axis passing through the polar pentagons. This requirement is necessary for finding the lowest set of locants by the procedure described above.



$R^1 = CH_2COOCH_2CH_3$
$R^2 = CH_2CH_3$

f) *71,71,74,74-Tetrakis[(ethoxycarbonyl)methyl] 72,72,73,73-Tetraethyl* (^{f}A)*-1,2:31,32:54,55:59,60-Tetrakis(methano)[70]fullerene-71,71,72,72,73,73,74,74-octacarboxylate* (the other enantiomer of **4**).

The stereochemical descriptions illustrated here for chiral C_{70} derivatives are generally applicable to chiral derivatives of other fullerenes, and this will be the subject of an upcoming report.

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[4] A. Herrmann, F. Diederich, C. Thilgen, H.-U. ter Meer, W.H. Müller, *Helv. Chim. Acta* **1994,** *77,* 1689.

An initial structural assignment of the five isomers again relied on the HPLC elution order. The compounds eluted first in fractions I and II should be the least polar isomers and, therefore, were assigned the least polar structures **7** and **8** or *vice versa*. By similar reasoning, structures **9** and **10** were assigned to the products in fractions III and IV or *vice versa* and structure **11** to the product in fraction V. This assignment found additional support by the fact that the obtained product quantities arising from fractions I and II, or fractions III and IV, respectively, were similar. Furthermore, the weight ratio for the five pure isomers from fractions I–V of 1.4:1:9.3:8.8:4.8 corresponds to a ratio of 1:7.5:2 for the three different constitutional isomers, and this ratio is similar to that seen in the formation of (±)-**1**, (±)-**2**, and **3** (*Sect. 2.1*). It can be expected with great confidence that the nucleophilic bis-attack by the anion of the optically active 2-bromomalonate **13b** shows the same preference for the C(56)–C(57) and C(59)–C(60) bonds as the attack of the anion formed by achiral **13a**.

The ^{1}H-NMR and IR spectra are very similar for mono-adduct **15** and for all five isomeric bis-adducts and, therefore, do not allow much distinction between the various compounds, except for stronger absorption bands at 1428, 578, and 533 cm^{-1} in the IR spectrum of the mono-adduct. In contrast, comparison between the ^{13}C-NMR spectra of the bis-adducts substantially strengthens the above structural assignments and also exhibits the expected similarities between pairs of isomers having the same constitution. Comparison of the aromatic and fullerene regions of the ^{13}C-NMR spectra (*Fig. 5*) shows that the spectra of fractions I and II (compounds **7** or **8**), as well as those of fractions III and IV (compounds **9** or **10**), are very similar pairwise, whereas the spectra of product fractions I, III, and V or of II, IV, and V display quite different patterns (*Fig. 5*). All five ^{13}C-NMR spectra show 35 resonances for the fullerene C-atoms (33 lines in the fullerene region between 130 and 160 ppm and 2 lines for the bridgehead sp^3-C-atoms at *ca.* 67 ppm), supporting the expected C_2-symmetry of all five bis-adducts. An additional six resonances between 126 and 129 ppm as well as two resonances around 139 ppm arise in each spectrum from the sp^2-C-atoms of the Ph rings. At this point, it cannot be determined which one of the two fractions I and II contains pure **7** or pure **8**, and, similarly, which one of fractions III and IV contains pure **9** or pure **10**.

The electronic absorption spectra of mono- (**15**) and bis-adducts (**7**–**11**) are dominated by the fullerene chromophore. Similarities between the UV/VIS spectra within the pairs of stereoisomers **7**/**8** or **9**/**10** are even larger than those seen in the ^{13}C-NMR spectral comparison. The nearly identical spectra measured for the pure compounds **7** and **8** in HPLC fractions I and II (or *vice versa*) and for pure **9** and **10** in fractions III and IV (or *vice versa*) are shown in *Fig. 6, a* and *b*. Significant differences, however, exist between the absorption spectra of the three constitutional isomers, which are shown in *Fig. 6, c*, together with the spectrum of mono-adduct **15**. All compounds have their onset of absorption between 700 and 720 nm and show a broad, more or less structured absorption between 350 and 550 nm. Characteristic for the bis-adduct **11** with the achiral fullerene chromophore, which is contained in the HPLC fraction V, is the short-wavelength band with a λ_{max} at 271 nm. This band appears at 270 nm in **3** containing the same C_{2v}-symmetrical fullerene functionalization pattern and is not observed for any of the other bis-adducts or for mono-adduct **15**.

The effect of the chiral functionalization pattern of the fullerene core is best visualized in the circular-dichroism (CD) spectra of the five bis-adducts **7**–**11** (*Fig. 7*). The CD

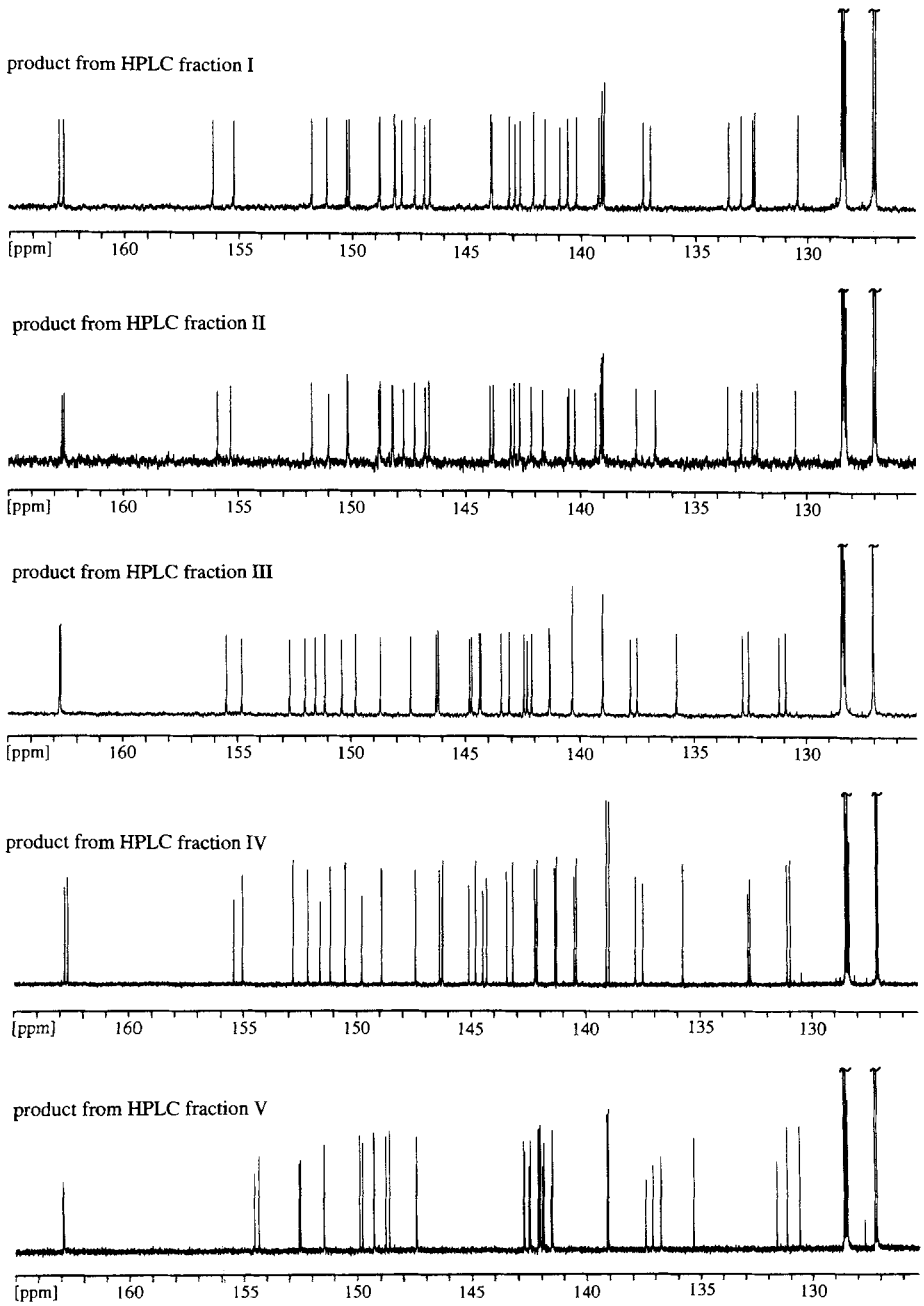


Fig. 5. *Comparison of the aromatic region of the* ^{13}C*-NMR spectra* (125.8 MHz, $CDCl_3$) *of the five isomeric* C_{70} *bis-adducts* **7**–**11**, *isolated from HPLC fractions I–V.* It cannot be determined, based on the available data, which one of the two fractions I and II contains pure **7** or pure **8**, and, similarly, which one of fractions III and IV contains pure **9** or pure **10**.

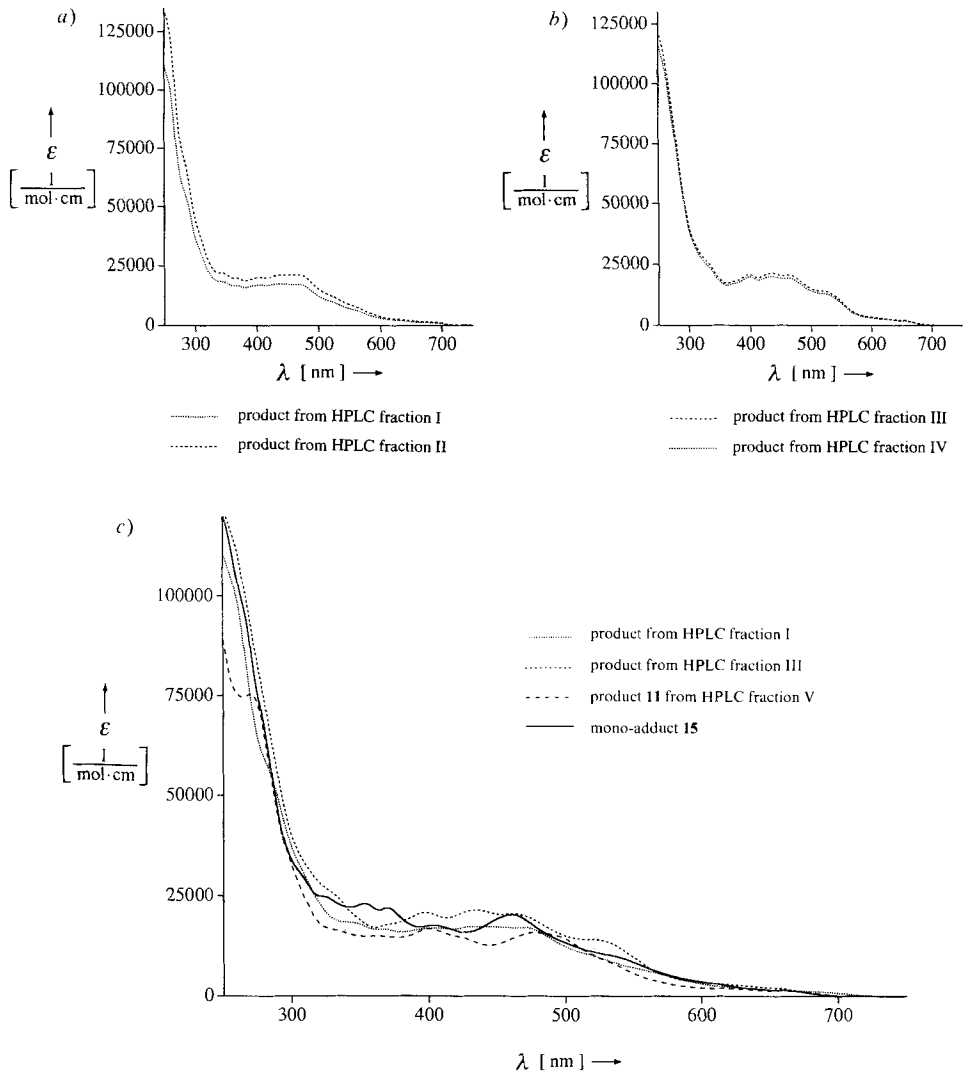


Fig. 6. *UV/VIS Spectra* (CH_2Cl_2) a) *of the pure isomers* **7** *and* **8** *of same constitution in the HPLC fractions I and II* (or *vice versa*), b) *of the pure isomers* **9** *and* **10** *of same constitution in fractions III and IV* (or *vice versa*), *and* c) *of the three pure constitutional isomers contained in fractions I, III, and V in comparison to the spectrum of mono-adduct* **15**

spectrum of **11**, isolated from HPLC fraction V, shows only weak *Cotton* effects (*Fig. 7, a*), since there exists no direct chiroptical contribution from the fullerene chromophore with its achiral (C_{2v}-symmetrical) functionalization pattern. We assign the $\Delta\varepsilon$ values below 400 nm to the chiroptical contributions of the chiral malonate addends and explain the weak *Cotton* effect above 550 nm with an induced circular dichroism originating from the perturbation of the achiral fullerene chromophore by the attached optically

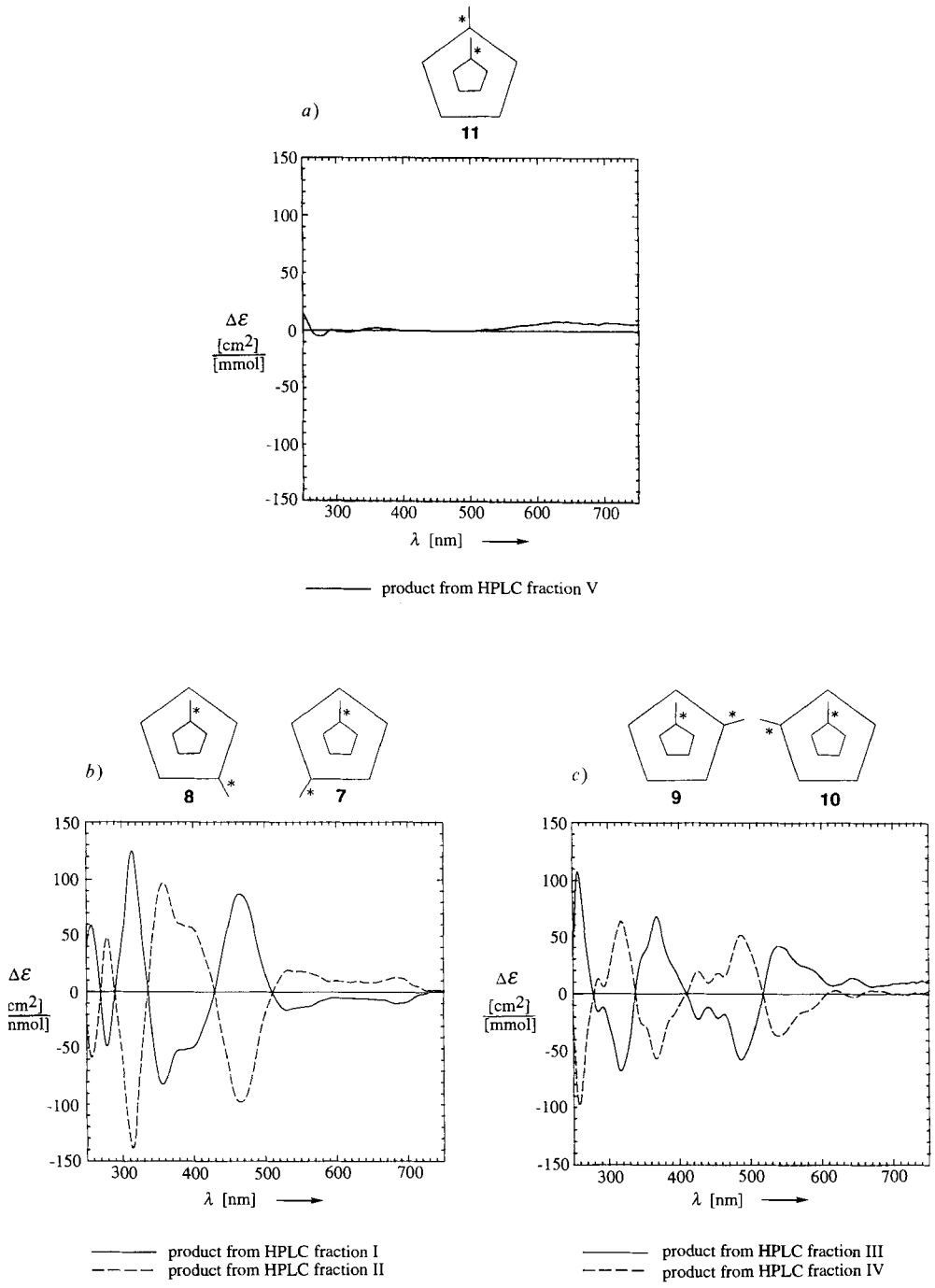
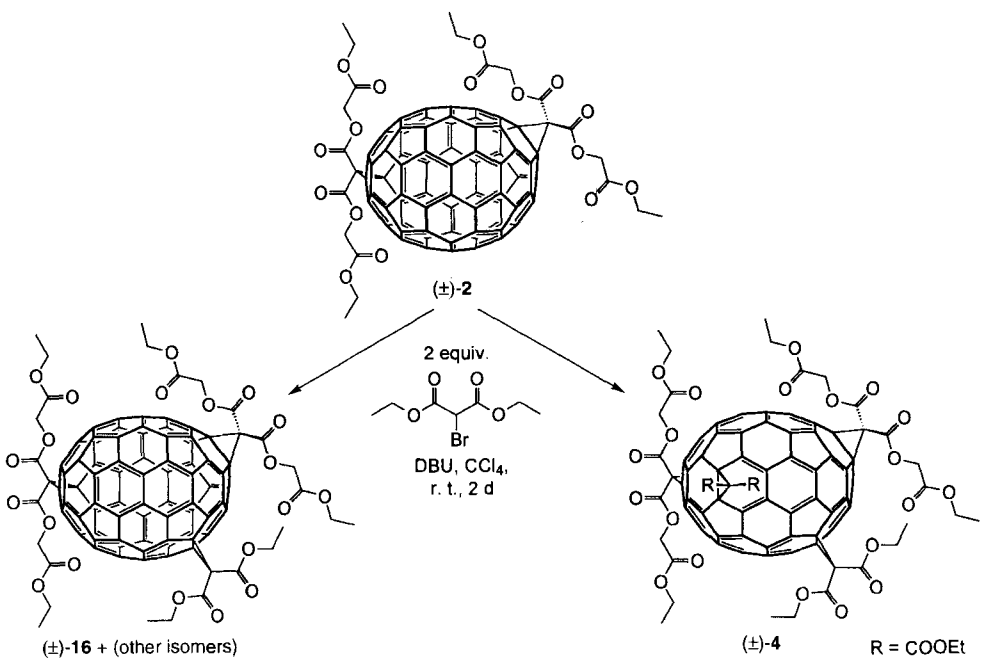


Fig. 7. *CD Spectra* (CH_2Cl_2) a) *of bis-adduct* **11**, b) *of bis-adducts* **7** *and* **8**, *and* c) *of bis-adducts* **9** *and* **10**

active addends. Much larger *Cotton* effects are recorded for isomers **7**–**10** (*Fig. 7, b* and *c*) due to strong chiroptical contributions from the chirally functionalized fullerene chromophores. The spectra clearly show that compounds **7** and **8**, and, similarly, compounds **9** and **10**, have the same constitution. Since the addition patterns on the fullerene surface in each of these two pairs of diastereoisomers have an enantiomeric relationship, their CD spectra closely resemble those expected for two enantiomers. Only at longer wavelength do the spectra of two diastereoisomers deviate from mirror image shapes, presumably as a result of the differential induced chiroptical effects resulting from the perturbation of the fullerene chromophore by the chiral addends. In analogy to the UV/VIS spectra (*Fig. 6*), the CD spectra of isomers **9** and **10** are more structured than those of isomers **7** and **8**.

2.3. *C_{70} Tris- and Tetrakis-adducts.* The two most abundant bis-adducts from the functionalization with the achiral malonate addends, C_2-symmetrical (±)-**2** and C_{2v}-symmetrical **3**, were further reacted with diethyl 2-bromomalonate to explore the regioselectivity in the formation of higher adducts. Diethyl 2-bromomalonate was chosen as reagent for the higher functionalization rather than the bulkier bis[(ethoxycarbonyl)-methyl] derivative **13a** to avoid steric hindrance of the ester groups in the multiple adducts. The higher functionalizations were performed in CCl_4 as solvent where the bis-adduct starting materials, in contrast to unfunctionalized C_{70}, were readily soluble. By performing the *Bingel* reaction in this apolar solvent, we expected higher regioselectivity and a reduction in the number of formed tris- and tetrakis-adducts, since the use of CCl_4 had previously led to a significant enhancement of the regioselectivity, as compared to

Scheme 4. *Synthesis of C_{70} Tris- and Tetrakis-adducts Starting from C_2-Symmetrical Bis-adduct* (±)-**2**



reactions in more polar solvents, in the cyclopropanation of a C_{60} tetrakis-adduct yielding C_{60} pentakis-adducts [9b].

When bis-adduct (±)-**2** was reacted for 2 d in CCl_4 with 2 equiv. of diethyl 2-bromomalonate and DBU, workup by column chromatography (silica gel *H*, CH_2Cl_2/AcOEt 98.5:1.5) yielded one tris- and one major tetrakis-adduct fraction in a weight ratio of *ca.* 1:2.6 (*Scheme 4*). ^{1}H- and ^{13}C-NMR Spectroscopy showed that the tris-adduct fraction consisted of a mixture of isomers, whereas from the major tetrakis-adduct fraction, a single isomer was isolated. MALDI-TOF (matrix-assisted laser-desorption-ionization time-of-flight) mass spectrometry suggested that a small, slower eluting fraction contained one or several other tetrakis-adduct isomers.

The ^{13}C-NMR spectrum of the tris-adduct fraction displays *ca.* 150 resonances in the fullerene region, indicating the presence of at least two isomers, probably with C_1 symmetry. Based on reactivity considerations discussed below as well as on its intermediacy in the formation of the isolated tetrakis-adduct, compound (±)-**16** should be one of these isomers. The presence of 31 resonances for the fullerene sp^2-C-atoms, four lines for the fullerene sp^3-C-atoms, six resonances for C=O as well as for CH_2 groups, and two signals for the methano bridge C-atoms in the ^{13}C-NMR spectrum (*Fig. 8, d*) reveals C_2 symmetry for the tetrakis-adduct which was assigned structure (±)-**4**. Addition of two diethylmalonate addends to (±)-**2** can generate several tetrakis-adducts with C_2 symmetry, and an unambiguous structural assignment based solely on ^{13}C-NMR spectral considerations is, therefore, not possible. The assignment of structure (±)-**4** to the isolated pure tetrakis-adduct is additionally based on bond-reactivity considerations discussed below (*Sect. 2.4*).

The C_{2v}-symmetrical bis-adduct **3** was reacted under similar conditions as those mentioned above (*Scheme 5*). This time, only 1 equiv. of bromomalonate was added, and the CCl_4 solution was left stirring at room temperature for 3 d. Column chromatography yielded 11% of C_s-symmetrical tris-adduct **5** and 18% of C_{2v}-symmetrical tetrakis-adduct **6** besides small amounts of, probably, higher adducts which were not further analyzed. The fact that, by using only 1 equiv. of bromomalonate, both the tris- and the tetrakis-adduct were formed, suggests that further functionalization of C_s-symmetrical tris-adduct **5** to give **6** occurred at least at the same rate than the attack at **3** to give **5**.

The ^{13}C-NMR spectrum of tris-adduct **5** (*Fig. 8, b*) displays 32 resonances in the fullerene sp^2-C-atom region. There are four signals for the bridgehead sp^3-C-atoms arising from the two addends already present in the C_{2v}-symmetrical bis-adduct starting material and one resonance with double intensity for the bridgehead sp^3-C-atoms connected to the third, diethyl malonate addend. The tris-adduct **5**, therefore, has C_s symmetry. This structural assignment is unambiguous, since, starting from the C_{2v}-symmetrical bis-adduct **3**, there is only one C_s-symmetrical tris-adduct structure possible, considering only additions to 6–6 bonds.

The C_{2v} symmetry of tetrakis-adduct **6** was readily deduced from the ^{13}C-NMR spectrum where only 18 signals appear for the fullerene sp^2-C-atoms, five of which show half intensity and are, therefore, assigned to the C-atoms on the equator of the fullerene (*Fig. 8, c*). Both the C=O and the CH_2 groups give four lines each. The fact that there are two signals for the bridgehead sp^3-C-atoms arising from the initial C_{2v}-symmetrical bis-functionalization in **3**, but only one signal with double intensity for the four newly formed bridgehead C-atoms necessitates that the third and fourth cyclopropanations

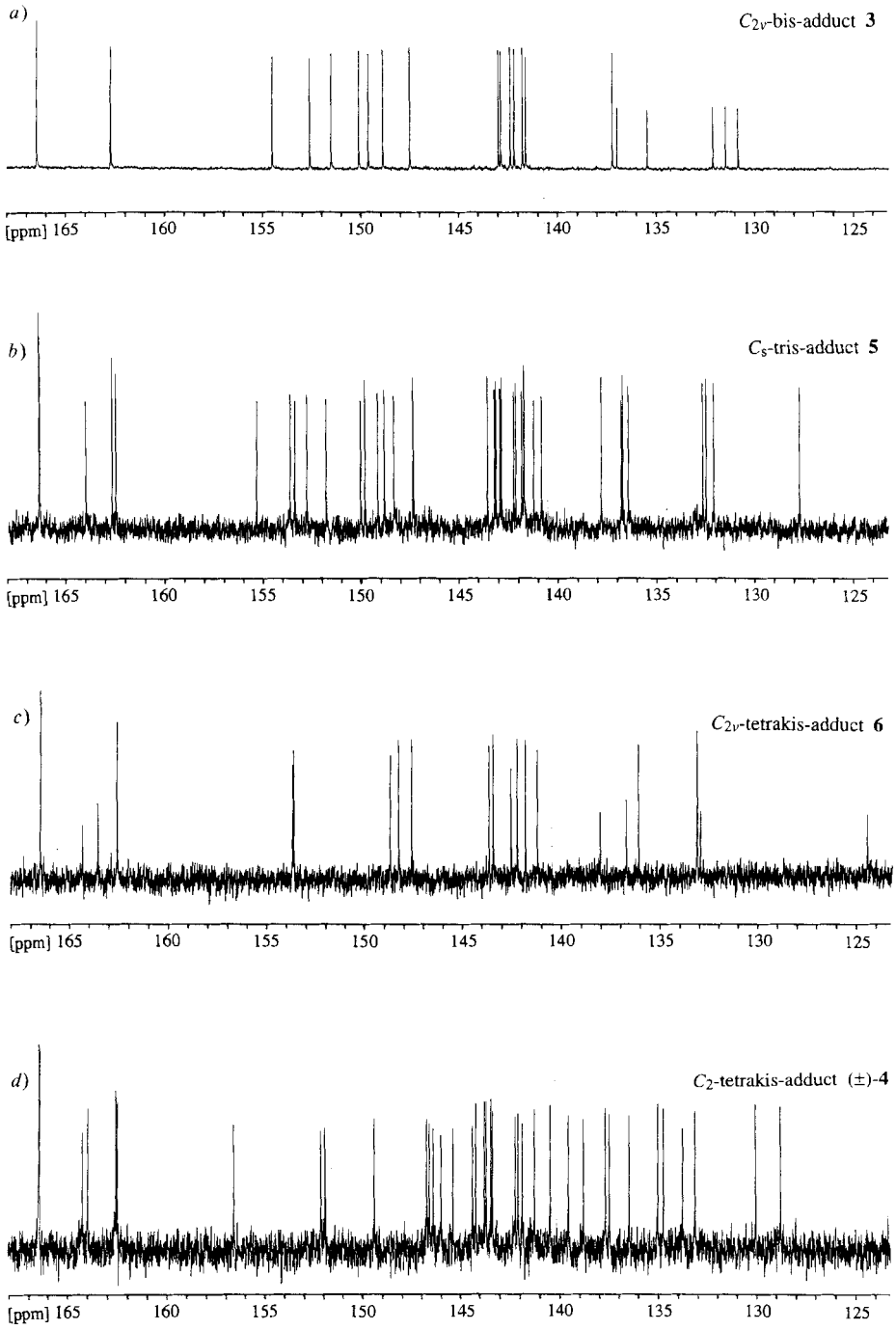
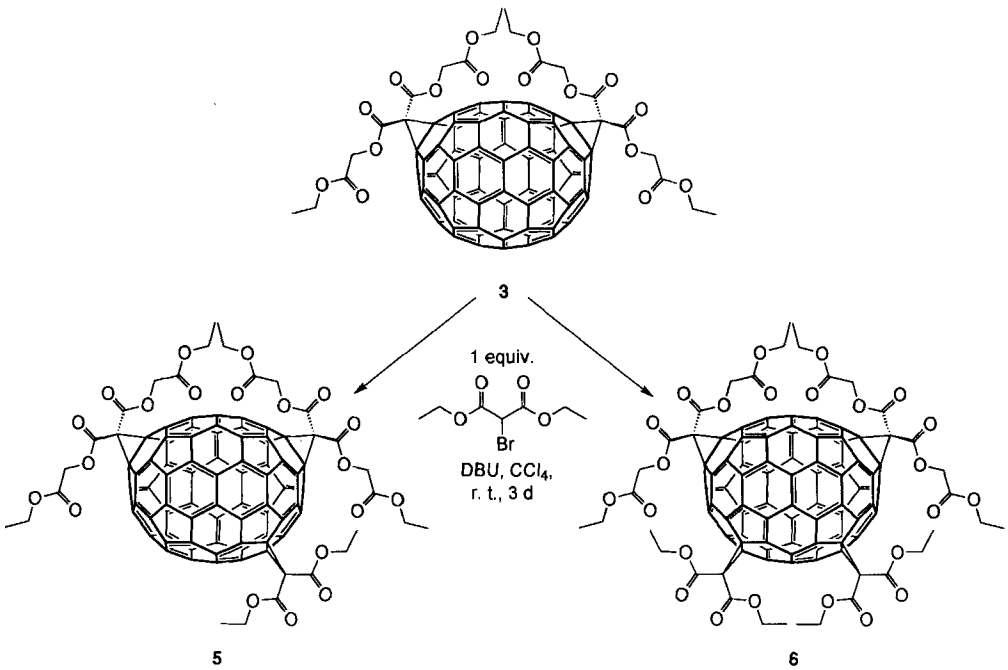


Fig. 8. *Expansions of the fullerene region of the* ^{13}C*-NMR spectra* (125.8 MHz, $CDCl_3$) *of* a) C_{70} *bis-adduct* **3**, b) *tris-adduct* **5**, c) *tetrakis-adduct* **6**, *and* d) *tetrakis-adduct* (±)-**4**

Scheme 5. *Synthesis of C_{70} Tris- and Tetrakis-adducts Starting from C_2-Symmetrical Bis-adduct* **3**



must have taken place at two bonds which are related to each other by a mirror plane as well as by a C_2 axis.

Starting from the C_{2v}-symmetrical bis-adduct **3**, there exists again only one unique arrangement for four addends at 6–6 bonds to give a C_{2v}-symmetrical tetrakis-adduct. The two additional malonates must have been added to β-type bonds; addition to further bonds of type α would only have given rise to tetrakis-adducts with at maximum C_2 symmetry. Therefore, as shown for structure **6**, the third and fourth cyclopropanations have taken place at the less reactive β-type bonds C(31)–C(32) and C(65)–C(66), a fact that may also explain the longer reaction times (3 d).

Based on the unambiguous structural assignments for the C_s-symmetrical tris-adduct **5** and C_{2v}-symmetrical tetrakis-adduct **6** and assuming similar reaction pathways in the functionalization of the bis-adduct starting materials, with the third and fourth additions taking place at β- rather than α-type bonds, the structure of the C_2-symmetrical tetrakis-adduct produced by starting from (±)-**2** can now be more confidently assigned as (±)-**4** (*Scheme 4*). The high yield of tetrakis-adduct (±)-**4** strongly suggests that one of the main tris-adducts produced corresponds to its direct, C_1-symmetrical precursor (±)-**16**.

The UV/VIS spectra of C_{2v}-symmetrical bis-adduct **3**, C_s-symmetrical tris-adduct **5**, and C_{2v}-symmetrical tetrakis-adduct **6** are shown in *Fig. 9*. The main differences between the three spectra can be observed between 250 and 300 nm, where **3** displays a maximum (270 nm), **5** a shoulder (262 nm), and **6** a maximum (258 nm) and a shoulder (289 nm). The onset of absorption occurs in a similar wavelength range between 700 and 720 nm.

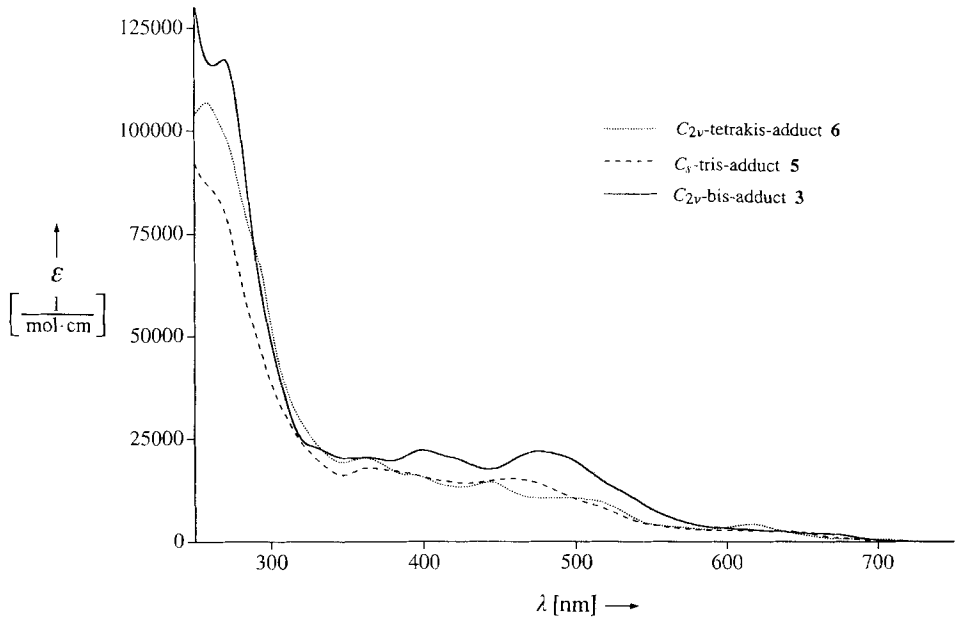


Fig. 9. *Comparison of the UV/VIS spectra* (CH_2Cl_2) *of* C_{70} *bis-adduct* **3**, *tris-adduct* **5**, *and tetrakis-adduct* **6**

The electronic absorption spectra of the two tetrakis-adducts (±)-**4** and **6** show some substantial differences. The onset of absorption moves hypsochromically from *ca.* 720 nm for **6** to *ca.* 675 nm for (±)-**4**. Both tetrakis-adducts show a weak maximum above 600 nm (628 nm for (±)-**4** and 617 nm for **6**) and a strong maximum around 260 nm (259 nm (ε = 150300) for (±)-**4** and 258 nm (ε = 107000) for **6**), with the molar extinction coefficient of tetrakis-adduct (±)-**4** being more than 40000 l mol^{-1} cm^{-1} higher at this maximum.

2.4. *Regioselectivity in Multiple Cyclopropanations of* C_{70}. A discussion of the regioselectivity must first consider that the average bond length and curvature at the unfunctionalized pole of a C_{70} mono-adduct are comparable to those in unfunctionalized C_{70} [13], and that both halves apparently react rather independently. The most curved α-type 6–6 bonds are preferentially attacked, and the first and second cyclopropanations take place at α-bonds at both poles of the fullerene yielding three constitutional isomers. Once the bis-adducts are formed, further addition must take place in a hemisphere already functionalized. However, attack at a second α-type bond in the same hemisphere apparently is unfavorable, presumably for both steric and electronic reasons. The experimental results described above indicate that C_{70} shows a similar pattern of second addition in the same hemisphere than observed for the bis-cyclopropanation of C_{60} [1] [7].

Considering that D_{5h}-C_{70} is built up of two halves of C_{60}, rotated by 180° and separated by an equatorial belt of 10 additional C-atoms, it is not surprising that there should be similarities in the regioselectivity of nucleophilic additions to both fullerenes, at least considering those reactions occurring in the same hemisphere of C_{70}. In the case of I_h-C_{60}, all 6–6 bonds are of type α. For the formation of higher adducts, it was observed

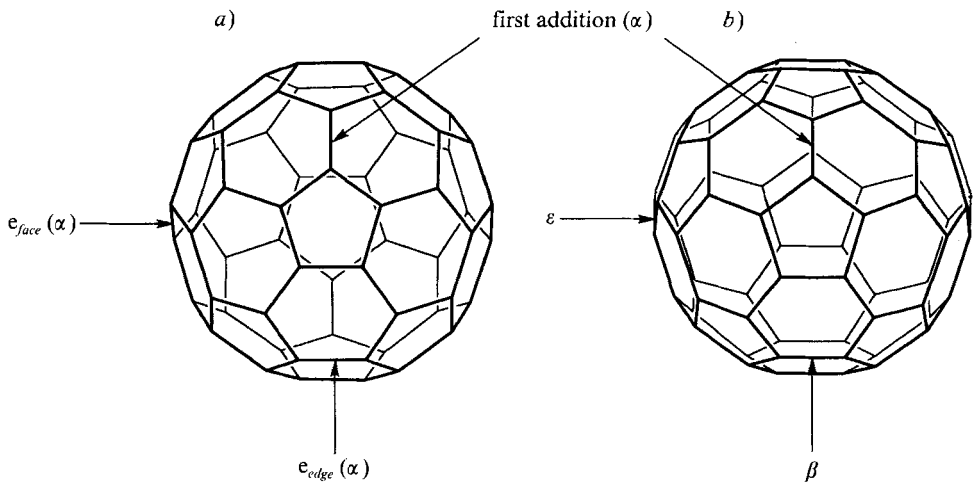


Fig. 10. *Comparison of the regioselectivity for the formation of higher adducts* a) *in* C_{60} *and* b) *in* C_{70}. If a first bridging addend in C_{60} is placed at the pole, the second addend preferentially enters in an equatorial (e) relation. The e_{face} bond sees the face of the bridging addend, whereas the e_{edge} bond sees its edge. In C_{70}, the second addition in the same hemisphere occurs preferentially at the β-type bond shown.

that the bonds e_{edge} and e_{face} (*Fig. 10*) lying on the equator of the molecule are more reactive than the other 6–6 bonds and that the second addition preferentially takes place at either one of these bonds [7]. If one now compares the observed addition pattern for the formation of the tris- and tetrakis-adducts of C_{70} with that known for bis-additions to C_{60}, one can see that the bond equivalent to the e_{edge} bond in C_{60} is of type β in C_{70} and, therefore, more reactive than the bond equivalent to the e_{face} bond in C_{60} which is of the less reactive type ε in C_{70} (*Fig. 10*). The fact that in C_{70} the bonds corresponding to the reactive e_{edge} and e_{face} bonds in C_{60} are of different reactivity may explain the observed high regioselectivity, yielding, *via* attack at β-type bonds, preferentially one tris- and one tetrakis-adduct.

3. Conclusion. – Cyclopropanation of C_{70} with achiral 2-bromomalonates in the *Bingel* reaction yielded predominantly one single mono-adduct (**14**) derived from reaction at the most curved 6–6 bond (type α) at the pole of the molecule where the pyramidalization of the sp^2-C-atoms is highest. Further addition occurred at the α-type bonds at the opposite pole and generated all three possible constitutionally isomeric bis-adducts in different ratios. Two of these constitutional isomers, (±)-**1** and (±)-**2**, are chiral (C_2 symmetry) as a result of the specific functionalization pattern on the fullerene core; the third constitutional isomer **3** is achiral (C_{2v} symmetry). The considerable preference for the formation of bis-adduct (±)-**2** suggests that the two α-type bonds C(56)–C(57) and C(59)–C(60) on the unfunctionalized pole are particularly activated towards nucleophilic attack by the first addend which is located on the opposite pole.

The use of C_2-symmetrical optically active malonate addends yielded, besides mono-adduct **15**, five optically active, C_2-symmetrical bis-adducts **7**–**11** formed by nucleophilic attack at the α-bonds on opposite poles. Compounds **7**/**8** and **9**/**10** are two constitutionally isomeric pairs of diastereoisomers, and, together with the third constitutional isomer

11, they all could be separated by prep. HPLC and fully characterized spectroscopically. The HPLC retention times as well as the ^{13}C-NMR, UV/VIS, and CD spectra showed close similarities for each pair of stereoisomers which was of great help in the structural assignment. The circular-dichroism (CD) spectra of stereoisomers **7** and **8**, and similarly of **9** and **10**, showed pronounced *Cotton* effects due to strong chiroptical contributions from the chirally functionalized fullerene chromophores. Since the addition patterns on the fullerene surface in each pair of diastereoisomers have an enantiomeric relationship, their CD spectra closely resemble those expected for two enantiomers and display near mirror-image-type shapes. In the third constitutional isomer **11**, the addition pattern on the fullerene surface is C_{2v}-symmetrical, and optical activity only results from the chiral addends; its CD spectrum shows weak *Cotton* effects mainly from induced circular dichroism originating presumably from the perturbation of the achiral fullerene chromophore by the attached chiral addends. Based on the numbering scheme for the C-atoms in C_{70} which has been worked out by *Taylor* [11a] and recommended to IUPAC, simple configurational descriptions for C_{70} derivatives which possess a chiral chromophore as a result of specific functionalization patterns are proposed. These descriptions can be generalized for all fullerenes, and this will be described in upcoming work.

Starting from the C_2-symmetrical bis-adduct (±)-**2**, the *Bingel* reaction with diethyl 2-bromomalonate yielded a mixture of tris-adducts and a pure tetrakis-adduct (±)-**4** with C_2 symmetry. In the further cyclopropanation of C_{2v}-symmetrical bis-adduct **3**, a C_s-symmetrical tris-adduct **5** and a C_{2v}-symmetrical tetrakis-adduct **6** were obtained. Whereas the structural assignment of (±)-**4** is based both on spectral data and considerations of the reactivity of the different types of 6–6 bonds against nucleophilic attack, the structural assignment of **5** and **6** was unambiguous, based solely on the spectral data.

A second addition in one hemisphere of a C_{70} bis-adduct does not occur at one of the four remaining free α-type bonds; apparently an addend at one of these bonds deactivates the others. The structures of the isolated tris- and tetrakis-adducts rather suggest that the preferred pattern for bis-functionalization within the same hemisphere of C_{70} is similar to that established for C_{60}. The second cyclopropanation of C_{60} occurs preferentially at α-type e_{edge} or e_{face} bonds on the equator. The corresponding bonds in a hemisphere of C_{70} are of different type (β and ε) and less reactive. Longer reaction times are needed for addition to these bonds, but as a result of the lower reactivity, selectivity is high and attack predominantly occurs at the more curved β-type bond closer to the pole. This study clearly demonstrates that the regioselectivity for the formation of tris- and tetrakis-adducts by nucleophilic cyclopropanation in apolar solvents is higher for C_{70} than for C_{60}. This conclusion should also hold for other nucleophilic additions and cycloadditions to C_{70}. Thus, highly functionalized C_{70} adducts such as (±)-**4** or **6** can be prepared without relying on HPLC separations or tether-controlled remote functionalization techniques, and this should increase the future interest in preparing tailor-made derivatives of C_{70} for potential materials or biological applications.

Note Added in Proof: *C. Bingel, H. Schiffer* (*Liebigs Ann.* **1995,** 1551) have recently reported independently the formation of three constitutional bis-adduct isomers corresponding to (±)-**1**, (±)-**2**, and **3** but with different malonate addends.

This work was supported by the *Swiss National Science Foundation* and *Hoechst AG*, Germany. We thank Prof. *Vladimir Prelog* for many discussions concerning configurational descriptions for chiral fullerene adducts. We are grateful to Mr. *Lyle Isaacs* for providing compound **13a**, Mr. *Thierry Granier* for assistance in measuring the CD spectra, Ms. *Francesca Cardullo* and Ms. *Ulrike Obst* for recording the ES mass spectra, Mr. *Hans-Ulrich Hediger* for recording the MALDI-TOF mass spectra, Mr. *Peter Kälin* from the *Kilolabor* (ETHZ) for charcoal extractions, and Ms. *Ester Martinborough*, Mr. *Martin Schreiber*, Mr. *Peter Wallimann*, Mr. *Berthold Hinzen*, Mr. *Ulf Neidlein*, and Mr. *Jens Cuntze* for NMR measurements.

Experimental Part

General. The syntheses of bis[(ethoxycarbonyl)methyl] propanedioate (**12a**) and bis[(ethoxycarbonyl)methyl] 2-bromopropanedioate (**13a**) are reported in [9b]. Reagents used were reagent-grade commercials. HPLC solvents were from *Biosolve*, *Fluka*, and *Merck*. Fullerene soot extract was purchased from *MER Corporation*, Tucson, Arizona, AZ 85706, USA; soot extract enriched in higher fullerenes was from *Hoechst AG*, Frankfurt am Main, Germany. CH_2Cl_2 and toluene used for the reactions were dried over molecular sieves (4 Å). Thin layer chromatography: *Polygram SIL G/UV$_{254}$* from *Macherey-Nagel*. Column chromatography (CC): silica gel (0.05–0.10 mm, 140–270 mesh) from *Macherey-Nagel* and silica gel *H* from *Fluka*. HPLC: *Regis Buckyclutcher I* Trident-Tri-DNP (5 μm), 250 mm × 4.6 mm i.d. or *Macherey-Nagel Nucleosil 100-7* silica gel (7 μm, 250 mm × 4 mm i.d., and 7 μm, 250 mm × 21 mm i.d.) columns; *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 were taken at r.t. with the detector wavelength fixed at 310 nm; anal. HPLC at flow rate 1 ml/min; injection volume, 20 μl of a CH_2Cl_2 or toluene soln. M.p.: all fullerene derivatives decomposed > 250°. UV/VIS Spectra: *Varian-CARY-5* spectrometer. CD Spectra: *Jasco J-710* spectropolarimeter. ^{1}H- and ^{13}C-NMR Spectra: *Bruker-AMX-500* and *Varian-GEMINI-200* and *-300* spectrometers. MS: MALDI-TOF spectra with reflectron detection (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) or α-cyano-4-hydroxycinnamic acid (CCA; 0.1M in MeCN/EtOH/H_2O 50:45:5 as matrix; electron spray (ES) spectra (positive mode) on a *Finnigan-TSQ-7000* spectrometer at 0 V, sample solns. in MeOH/NH_4OAc (10 mM in H_2O) 2:1.

1. *Purification of C_{70}.* C_{70} used for the additions was either purified by HPLC as reported previously [12e] or isolated by column chromatography. For the latter procedure, crude fullerene extract was loaded on a mixture of activated charcoal and silica gel as described in [18]. Elution with toluene gave pure C_{60}, whereas the higher fullerenes and parts of C_{60} remained adsorbed on the stationary phase. Extraction of the stationary phase with 1,2-dichlorobenzene by sonication at 40° and filtration gave, after several re-extraction cycles, a crude fullerene mixture enriched in C_{70} (61%, as shown by the integrated HPLC peak areas in a separation on a *Buckyclutcher I* column using hexane/toluene 60:40, with optical detection at 310 nm). Further purification of C_{70} was carried out following a procedure developed by *Tour* and coworkers [19]. The single-column purification of 845 mg extract (*Norit A* (*Aldrich*), toluene/1,2-dichlorobenzene 1:1, then pure 1,2-dichlorobenzene) afforded 6 fractions with the following compositions (determined by HPLC): *Fraction 1* consisted of 205 mg of pure C_{60}, *Fr. 2* gave 231 mg of C_{60}/C_{70} 38:62, *Fr. 3* 101 mg of C_{70} (88% purity), *Fr. 4* 66 mg of C_{70} (92% purity), *Fr. 5* 131 mg of C_{70} (96% purity), and *Fr. 6* 57 mg of C_{70} (94% purity). Fractions with a C_{70} content higher 90% were used for the additions.

2. *Reaction of C_{70} and* **13a**. 2.1. *Bis[(ethoxycarbonyl)methyl] 1,2-Methano[70]fullerene-71,71-dicarboxylate* (**14**). DBU (18.1 mg, 0.119 mmol) in toluene (5 ml) was added to a soln. of C_{70} (100.0 mg, 0.119 mmol) and **13a** (1 equiv., 43.0 mg, 0.119 mmol) in toluene (100 ml). After 1 h, the mixture was concentrated to *ca.* 10 ml and chromatographed (SiO_2, CH_2Cl_2) to recover unreacted C_{70} and **14**. Elution with CH_2Cl_2/AcOEt 98.5:1.5 yielded (±)-**1**, (±)-**2**, and **3**. Recrystallization from CH_2Cl_2/cyclohexane followed by drying at 25°/10^{-1} Torr gave **14** (62.5 mg, 47%) and (±)-**1**, (±)-**2**, and **3** (total yield: 16.9 mg, 10%) as black solids. **14**: R_f (CH_2Cl_2) 0.46. UV/VIS (CH_2Cl_2): 607 (sh, 3300), 535 (sh, 14700), 460 (22200), 403 (19000), 369 (23500), 352 (25100), 328 (sh, 27100), 323 (27600), 308 (sh, 33000), 260 (sh, 119700). IR (KBr): 2972*w*, 1752*s*, 1428*s*, 1376*w*, 1293*w*, 1274*w*, 1197*s*, 1159*m*, 1097*m*, 1031*m*, 795*w*, 672*w*, 578*m*, 533*m*, 457*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.96 (*s*, 4 H); 4.30 (*q*, *J* = 7.1, 4 H); 1.33 (*t*, *J* = 7.1, 6 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 166.37 (C=O); 162.48 (C=O); 155.04; 151.32; 151.30; 151.13; 150.68; 150.55; 149.31; 149.24; 149.10; 148.78; 148.58; 148.47; 148.45; 147.53; 147.48; 147.27; 146.98; 146.45; 145.95; 145.87; 144.91; 143.93; 143.82; 143.55; 142.85; 142.41 (2 ×); 141.56; 140.99; 136.51; 133.53; 132.79; 130.95; 130.94; 130.79; 66.46 (fullerene sp^3-C); 65.99 (fullerene sp^3-C); 62.77 (CH_2); 61.86 (CH_2); 35.99 (methano bridge); 14.22 (2 Me). FAB-MS: 1115.0 (M^+), 839.9 (C_{70}^+).

2.2. *C_{70} Bis-adducts (±)-**1**, (±)-**2**, and **3**. Method 1:* As described in *2.1*, with DBU (73.0 mg, 0.480 mmol), toluene (5 ml), C_{70} (201.6 mg, 0.239 mmol), **13a** (2 equiv., 170.3 mg, 0.480 mmol), and toluene (200 ml): bis-adducts (228.4 mg, 69%) as black solid.

Method 2: As described in *2.1*, with DBU (4.1 mg, 0.027 mmol), toluene (5 ml), **14** (30.0 mg, 0.027 mmol), **13a** (1 equiv., 9.6 mg, 0.027 mmol), and toluene (30 ml): 2 mg (7%) of unreacted **14** and 28 mg (75%) of a mixture of bis-adducts as black solid. The mixture of bis-adducts (170.0 mg) was separated by CC (SiO_2 *H*, CH_2Cl_2). Recrystallization from CH_2Cl_2/cyclohexane followed by drying at 25°/10^{-1} Torr gave (±)-**1** (13.0 mg, 10%), (±)-**2** (79.3 mg, 62%), and **3** (36.6 mg, 28%) as black solids which did not melt below 250°.

Tetrakis[(ethoxycarbonyl)methyl] 1,2:67,68-Bis(methano)[70]fullerene-71,71,72,72-tetracarboxylate ((±)-**1**): R_f (CH_2Cl_2) 0.18. UV/VIS (CH_2Cl_2): 678 (sh, 1500), 635 (sh, 2700), 515 (sh, 14500), 467 (23200), 435 (sh, 22900), 401 (21800), 367 (21700), 282 (sh, 77000), 256 (sh, 138000). IR (KBr): 2978*w*, 2922*w*, 2847*w*, 1751*s*, 1447*m*, 1424*m*, 1378*m*, 1297*m*, 1275*m*, 1199*s*, 1174*m*, 1163*m*, 1100*m*, 1071*w*, 1031*m*, 938*w*, 856*w*, 814*w*, 794*w*, 736*w*, 721*w*, 702*w*, 672*w*, 579*w*, 536*w*, 456*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.96 (*s*, 4 H); 4.95 (*s*, 4 H); 4.30 (*q*, J = 7.2, 4 H); 4.30 (*q*, J = 7.2, 4 H); 1.33 (*t*, J = 7.2, 6 H); 1.32 (*t*, J = 7.2, 6 H). ^{13}C-NMR (125.8 MHz,$CDCl_3$): 166.34 (C=O); 166.33 (C=O); 162.47 (C=O); 162.33 (C=O); 156.04; 155.34; 151.87; 151.18; 150.31; 150.28; 149.05; 148.96; 148.46; 148.35; 148.05; 147.39; 146.98; 146.90; 144.10; 144.02; 143.47; 143.01; 142.83; 142.49; 141.82; 140.66; 140.63; 140.59; 139.52; 139.03; 137.20; 136.60; 133.61; 133.09; 132.56; 132.51; 130.77; 67.24 (fullerene sp^3-C); 66.66 (fullerene sp^3-C); 62.73 (CH_2); 62.71 (CH_2); 61.78 (2 CH_2); 35.61 (methano bridge); 14.18 (2 Me). MALDI-TOF-MS (CCA): 1388.7 (M^+), 1316.5 ([M – C_4H_9O]$^+$), 1286.4.

Tetrakis[(ethoxycarbonyl)methyl] 1,2:56,57-Bis(methano)[70]fullerene-71,71,72,72-tetracarboxylate ((±)-**2**). R_f (CH_2Cl_2) 0.18. UV/VIS (CH_2Cl_2): 635 (sh, 1900), 525 (sh, 15100), 461 (22400), 433 (23100), 396 (22200), 331 (sh, 26800), 306 (sh, 37100), 255 (sh, 129400). IR (KBr): 2978*w*, 2922*w*, 2850*w*, 1753*s*, 1443*m*, 1425*m*, 1378*m*, 1296*m*, 1276*m*, 1197*s*, 1160*m*, 1099*m*, 1031*m*, 856*w*, 794*w*, 725*w*, 669*w*, 579*w*, 546*w*, 457*w*, 419*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.96 (*s*, 4 H); 4.95 (*s*, 4 H); 4.30 (*q*, J = 7.2, 4 H); 4.28 (*q*, J = 7.2, 4 H); 1.32 (*t*, J = 7.2, 6 H); 1.31 (*t*, J = 7.2, 6 H). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 163.39 (2 C=O); 162.97 (C=O); 162.88 (C=O); 155.93; 155.41; 153.45; 152.55; 152.07; 151.64; 150.88; 150.45; 149.46; 147.90; 146.96; 146.81; 146.65; 145.28; 145.11; 144.96; 144.85; 144.02; 143.84; 143.06; 142.61; 142.48; 142.08; 141.86; 141.20; 140.82; 137.86; 137.81; 136.21; 133.34 (2 ×); 131.88; 131.52; 67.11 (fullerene sp^3-C); 66.83 (fullerene sp^3-C); 63.05 (CH_2); 62.11 (CH_2); 37.21 (methano bridge); 14.42 (Me). MALDI-TOF-MS (CCA): 1389.0 (M^+), 1286.8.

Tetrakis[(ethoxycarbonyl)methyl] 1,2:41,58-Bis(methano)[70]fullerene-71,71,72,72-tetracarboxylate (**3**). R_f (CH_2Cl_2) 0.18. UV/VIS (CH_2Cl_2): 666 (sh, 2000), 613 (sh, 3000), 528 (sh, 12500), 476 (21900), 424 (sh, 19900), 399 (22300), 361 (20500), 326 (sh, 23300), 270 (117400). IR (KBr): 2928*w*, 2850*w*, 1753*s*, 1633*w*, 1425*w*, 1378*w*, 1294*m*, 1275*m*, 1197*s*, 1175*m*, 1100*m*, 1033*m*, 856*w*, 794*w*, 725*w*, 703*w*, 663*w*, 578*w*, 500*w*, 456*w*, 422*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.98 (*s*, 8 H); 4.30 (*q*, J = 7.2, 8 H); 1.33 (*t*, J = 7.2, 12 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 166.42 (C=O); 162.62 (C=O); 154.44; 152.53; 151.45; 150.08; 149.58; 148.86; 147.46; 142.93; 142.81; 142.31; 142.12; 141.70; 141.54; 137.06; 136.83; 135.29; 131.95; 131.32; 130.68; 66.14 (fullerene sp^3-C); 65.78 (fullerene sp^3-C); 62.82 (CH_2); 61.87 (CH_2); 35.57 (methano bridge); 14.15 (Me). FAB-MS: 1389.1 (M^+), 839.9 (C_{70}^+).

3. *Addition of Bis[(S)-1-phenylbutyl] 2-Bromopropanedioate* (**13b**) *to* C_{70}. 3.1. *Bis[(S)-1-phenylbutyl] Propanedioate* (**12b**). Pyridine (1.05 ml, 130 mmol) was added to a soln. of (*S*)-1-phenylbutanol (2.015 g, 134 mmol) in dry CH_2Cl_2 (50 ml), and the mixture was purged with Ar and cooled with an ice bath. Propanedioyl dichloride (0.65 ml, 67 mmol) was added dropwise within 10 min (→ dark-orange). After 2½ h, the ice bath was removed and the soln. stirred at r.t. overnight. The violet soln. was extracted with H_2O and the org. phase turned dark green. CC (SiO_2/CH_2Cl_2) gave **12b** (2.218 g, 90%). Orange-yellow oil. R_f (CH_2Cl_2) 0.53. $[\alpha]_D^{22} = -82.3$ (c = 0.92, $CHCl_3$). IR (neat): 3088*w*, 3064*w*, 3033*w*, 2958*m*, 2936*w*, 2872*w*, 1749*s*, 1733*s*, 1605*w*, 1584*w*, 1494*w*, 1454*w*, 1337*w*, 1311*w*, 1262*m*, 1202*w*, 1174*w*, 1150*m*, 1101*w*, 1054*w*, 1022*w*, 978*w*, 915*w*, 846*w*, 759*m*, 698*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.50–7.20 (*m*, 10 H); 5.89 (*dd*, J = 7.8, 6.3, 2 H); 3.43 (*s*, 2 H); 2.08–1.70 (*m*, 4 H); 1.57–1.16 (*m*, 4 H); 0.97 (*t*, J = 7.3, 6 H). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 166.22; 140.63; 128.86; 128.41; 126.99; 77.48; 42.42; 38.58; 18.96; 14.03. ES-MS: 386.3 ([M + NH_4]$^+$), 133.1 ($PhC_4H_8^+$).

3.2 *Bis[(S)-1-phenylbutyl] 2-Bromopropanedioate* (2 diastereoisomers; **13b**) *and Bis[(S)-1-phenylbutyl] 2,2-Dibromopropanedioate.* DBU (0.67 ml, 45 mmol) was added to **12b** (1.386 g, 38 mmol) in THF (20 ml), and the soln. was cooled to −78° under Ar. CBr_4 (1.2 equiv., 1.486 g, 45 mmol) in 5 ml THF was added (→ deep yellow) and the mixture stirred for 30 min, quenched with 0.1M HCl (*ca.* 20 ml), and brought to r.t. Et_2O was added and the org. phase extracted with 0.1M HCl, sat.aq. $NaHCO_3$ (to pH *ca.* 6), and NaCl solns. CC (SiO_2, hexane/CH_2Cl_2 2:1) gave **13b** (0.287 g, 17%) and *bis[(S)-1-phenylbutyl] 2,2-dibromopropanedioate* (0.779 g, 40%) as yellow oils as well as 0.206 g of a mixed fraction containing the two products in a ratio of 1:0.9.

13b: R_f (CH_2Cl_2/hexane 1:1) 0.34. $[\alpha]_D^{22} = -85.4$ (c = 0.93, $CHCl_3$). IR (neat): 3089*w*, 3064*w*, 3033*w*, 2961*s*, 2934*m*, 2872*m*, 1761*s*, 1742*s*, 1605*w*, 1586*w*, 1495*w*, 1454*m*, 1333*m*, 1282*s*, 1243*s*, 1202*m*, 1145*s*, 1100*m*, 1053*w*,

1020*w*, 932*w*, 760*m*, 698*s*, 653*w*, 622*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.44–7.31 (*m*, 10 H); 5.93 (*dd*, *J* = 7.8, 6.1, 1 H); 5.90 (*dd*, *J* = 7.8, 6.1 1 H); 4.95 (*s*, 1 H); 2.07–1.93 (*m*, 2 H); 1.91–1.76 (*m*, 2 H); 1.52–1.27 (*m*, 4 H); 0.99 (*t*, *J* = 7.4, 3 H); 0.97 (*t*, *J* = 7.4, 3 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 163.61; 163.24; 139.11; 139.07; 128.17; 128.16; 127.89; 127.87; 126.18; 126.15; 78.75; 78.60; 42.67; 37.85; 37.80; 18.29; 18.23; 13.43; 13.41. ES-MS: 464.3 ($[M + NH_3]^+$), 132.9 ($PhC_4H_8^+$).

Bis[(S)-1-phenylbutyl] 2,2-Dibromopropanedioate. R_f (CH_2Cl_2/hexane 1:1) 0.23. $[\alpha]_D^{22} = -80.5$ (*c* = 0.98, $CHCl_3$). IR (neat): 3088*w*, 3063*w*, 3032*m*, 2960*s*, 2932*s*, 2871*m*, 1755*s*, 1736*s*, 1604*w*, 1586*w*, 1496*m*, 1456*m*, 1381*w*, 1331*w*, 1244*s*, 1201*s*, 1158*w*, 1102*m*, 1073*w*, 1052*m*, 1022*m*, 967*m*, 931*m*, 914*m*, 889*w*, 852*w*, 828*w*, 759*m*, 698*s*, 641*w*, 617*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.45–7.25 (*m*, 10 H); 5.84 (*dd*, *J* = 7.7, 6.1, 2 H); 2.10–1.70 (*m*, 4 H); 1.55–1.10 (*m*, 4 H); 0.95 (*t*, *J* = 7.3, 6 H). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 162.82; 139.23; 128.88; 128.71; 126.81; 81.26; 51.67; 38.40; 18.76; 13.95. ES-MS: 544.1 ($[M + NH_4]^+$), 133.0 ($PhC_4H_8^+$).

3.3. *Bis[(S)-1-phenylbutyl] 1,2-Methano[70]fullerene-71,71-dicarboxylate* (**15**) *and Bis-adducts* **7**–**11**. A soln. of C_{70} (80 mg, 0.095 mmol) in dry toluene (90 ml) was sonicated and purged with Ar after which **13b** (0.066 g, 0.146 mmol) and DBU (0.022 g, 0.143 mmol), each dissolved in toluene, were added. The soln. was stirred overnight at r.t. The concentrated mixture was chromatographed (SiO_2, hexane/CH_2Cl_2 2:1): **15** (22 mg, 19%), **7**–**11** (100 mg, 67%), and small amounts of, probably, higher adducts as black solids. The mono-adduct fraction was dissolved in CH_2Cl_2 and precipitated with EtOH at 4°, washed with pentane, filtered over a small plug (SiO_2, benzene), and crystallized by vapor diffusion of pentane into a concentrated soln. of benzene to give 12.9 mg of pure **15**. R_f (CH_2Cl_2/hexane 1:1) 0.53. UV/VIS (CH_2Cl_2): 672 (sh, 1100), 606 (sh, 3300), 542 (sh, 9400), 461 (20300), 403 (17700), 370 (22000), 353 (23000), 326 (sh, 24600). CD (CH_2Cl_2): 620 ($\Delta\varepsilon$ = 2), 375 (2), 303 (−2), 276 (−3). IR (KBr): 2952*m*, 2924*m*, 2865*w*, 1741*s*, 1493*w*, 1454*m*, 1428*s*, 1415*m*, 1376*w*, 1268*m*, 1249*m*, 1226*s*, 1177*w*, 1161*w*, 1136*w*, 1093*m*, 1051*w*, 1031*w*, 957*w*, 929*w*, 795*w*, 757*w*, 696*s*, 672*w*, 578*m*, 533*m*, 458*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.49–7.22 (*m*, 10 H); 6.06–6.01 (*m*, 2 H); 2.19–2.08 (*m*, 2 H); 2.00–1.90 (*m*, 2 H); 1.59–1.35 (*m*, 4 H); 1.02 (*t*, *J* = 7.4, 3 H); 0.98 (*t*, *J* = 7.4, 3 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 162.72 (C=O); 162.66 (C=O); 155.13; 154.97; 151.32; 151.31; 151.25; 151.14 (2 ×); 150.68; 150.66; 150.55 (2 ×); 149.28; 149.27; 149.19 (2 ×); 149.06; 149.02; 148.63; 148.52; 148.47 (2 ×); 148.43 (2 ×); 148.38; 148.35; 147.50; 147.48 (2 ×); 147.25 (2 ×); 146.96 (2 ×); 146.42; 145.87 (2 ×); 145.84; 145.80; 144.86; 144.72; 143.89 (2 ×); 143.79; 143.76; 143.45 (2 ×); 142.87; 142.75; 142.75; 142.51; 142.07; 141.99; 141.53; 141.48; 140.64; 140.53; 138.99 (arom. C); 138.91 (arom. C); 136.89; 136.60; 133.51; 133.46; 132.78; 132.77; 130.86; 130.84; 130.82; 130.75 (2 ×); 130.71; 128.59 (arom. CH); 128.57 (arom. CH); 128.50 (arom. CH); 128.46 (arom. CH); 127.22 (arom. CH); 127.15 (arom. CH); 79.77 (Ph*C*HO); 79.73 (Ph*C*HO); 66.81 (fullerene sp^3-C); 66.13 (fullerene sp^3-C); 37.79 (2 CH_2); 37.44 (methano bridge); 18.87 (CH_2); 18.84 (CH_2); 13.80 (Me); 13.76 (Me); 29.66 (impurity). MALDI-TOF-MS (DHB): 1206.2 (M^-), 1031.6, 898.9, 880.5, 852.8, 839.6 (C_{70}^-).

The bis-adduct fraction was separated by prep. HPLC (SiO_2). An average of 8 mg of bis-adduct in CH_2Cl_2/hexane 1:1 (800–1000 µl) was injected onto the column and eluted with hexane/toluene 65:35 at a flow rate of 30 ml/min. Five fractions (I–V) were collected. Fr. I–II were dissolved in CH_2Cl_2/hexane 1:1 (*ca.* 3 ml) and re-injected under the same conditions each. Fr. I (5.2 mg, 4%), II (3.7 mg, 3%), III (34.4 mg, 23%), IV (32.6 mg, 22%), and V (17.7 mg, 12%) 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 spectroscopy after prolonged drying.

Tetrakis[(S)-1-phenylbutyl] (^{1}C)- and (^{1}A)-1,2:67,68-Bis(methano)[70]fullerene-71,71,72,72-tetracarboxylate (**7** and **8**): *Product of HPLC fraction I:* R_f (CH_2Cl_2/hexane 1:1) 0.40. UV/VIS (CH_2Cl_2): 698 (sh, 800), 468 (17100), 446 (17300), 402 (17000), 364 (sh, 16700), 347 (sh, 18200), 284 (sh, 55900), 259 (sh, 100900). CD (CH_2Cl_2): 740 ($\Delta\varepsilon$ = 2), 685 (−10), 597 (−5), 531 (−16), 465 (87), 381 (−52), 357 (−82), 314 (125), 279 (−48), 256 (59). IR (KBr): 2954*m*, 2923*m*, 2867*w*, 1742*s*, 1494*w*, 1448*m*, 1426*m*, 1414*w*, 1378*w*, 1270*m*, 1242*s*, 1224*s*, 1174*m*, 1166*m*, 1096*m*, 1051*w*, 1028*w*, 930*w*, 795*w*, 757*w*, 738*w*, 696*s*, 673*w*, 580*w*, 535*m*, 458*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.45–7.17 (*m*, 20 H); 6.01–5.96 (*m*, 4 H); 2.15–2.02 (*m*, 4 H); 1.95–1.82 (*m*, 4 H); 1.60–1.20 (*m*, 8 H); 0.97 (*t*, *J* = 7.4, 6 H); 0.94 (*t*, *J* = 7.3, 6 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 162.79 (C=O); 162.60 (C=O); 156.10; 155.21; 151.81; 151.14; 150.27; 150.16; 148.86; 148.81; 148.19; 148.16; 147.86; 147.27; 146.84; 146.60; 143.91; 143.86; 143.12; 142.86; 142.63; 142.04; 141.53; 140.89; 140.53; 140.15; 139.16; 139.04 (arom. C); 138.95; 138.92 (arom. C); 137.21; 136.89; 133.48; 132.94; 132.43; 132.35; 130.46; 128.57 (arom. CH); 128.52 (arom. CH); 128.47 (arom. CH); 128.40 (arom. CH); 127.20 (arom. CH); 127.10 (arom. CH); 79.64 (Ph*C*HO); 79.61 (Ph*C*HO); 67.46 (fullerene sp^3-C); 66.70 (fullerene sp^3-C); 37.81 (2 CH_2); 36.84 (methano bridge); 18.85 (CH_2); 18.82 (CH_2); 13.79 (Me); 13.76 (Me); 29.66 (impurity). MALDI-TOF-MS (CCA): 1573.3 (M^+), 1441.5.

Product of HPLC fraction II: R_f (CH_2Cl_2/hexane 1:1) 0.40. UV/VIS (CH_2Cl_2): 695 (sh, 1200), 469 (21200), 453 (21200), 402 (20100), 365 (sh, 19900), 343 (sh, 22000), 284 (sh, 68500), 260 (sh, 121900). CD (CH_2Cl_2): 734 ($\Delta\varepsilon$ = 2), 684 (13), 597 (10), 531 (19), 464 (−98), 381 (61), 357 (97), 314 (−139), 279 (48), 257 (−58). IR (KBr):

2955*m*, 2921*m*, 2866*w*, 2852*w*, 1741*s*, 1494*w*, 1448*m*, 1426*m*, 1413*w*, 1377*w*, 1269*m*, 1242*s*, 1223*s*, 1173*m*, 1164*m*, 1096*m*, 1049*w*, 1028*w*, 930*w*, 795*w*, 756*w*, 738*w*, 696*s*, 671*w*, 580*w*, 534*m*, 458*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.47–7.20 (*m*, 20 H); 6.03–5.98 (*m*, 4 H); 2.17–2.02 (*m*, 4 H); 1.97–1.83 (*m*, 4 H); 1.60–1.15 (*m*, 8 H); 1.01 (*t*, *J* = 7.4, 6 H); 0.95 (*t*, *J* = 7.4, 6 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 162.69 (C=O); 162.61 (C=O); 155.94; 155.38; 151.84; 151.09; 150.26; 150.24; 148.84; 148.78; 148.27; 148.23; 147.77; 147.28; 146.81; 146.65; 143.94; 143.79; 143.04; 142.88; 142.64; 142.13; 141.62; 140.54; 140.48; 140.21; 139.30; 139.09; 139.04 (arom. C); 138.97 (arom. C); 137.49; 136.66; 133.53; 132.92; 132.45; 132.23; 130.59; 128.54 (arom. CH); 128.48 (arom. CH); 128.45 (arom. CH); 128.37 (arom. CH); 127.17 (arom. CH); 127.07 (arom. CH); 79.62 (Ph*C*HO); 79.61 (Ph*C*HO); 67.50 (fullerene sp^3-C); 66.74 (fullerene sp^3-C); 37.84 (CH_2); 37.79 (CH_2); 36.94 (methano bridge); 18.83 (CH_2); 18.79 (CH_2); 13.76 (Me); 13.72 (Me); 29.64 (impurity). MALDI-TOF-MS (DHB): 1572.1 (M^-), 1396.5, 865.3, 852.2, 839.2 (C_{70}^-).

Tetrakis[(S)-1-phenylbutyl] (^{f}A)- and (^{f}C)-1,2:56,57-Bis(methano)[70]fullerene-71,71,72,72-tetracarboxylate (**9** and **10**): *Product of HPLC fraction III:* R_f (CH_2Cl_2/hexane 1:1) 0.40. UV/VIS (CH_2Cl_2): 652 (2100), 529 (13700), 461 (20600), 434 (21400), 397 (20800), 370 (sh, 17900), 331 (sh, 25400). CD (CH_2Cl_2): 671 ($\Delta\varepsilon$ = 6), 643 (14), 615 (7), 572 (sh, 24), 540 (42), 486 (−58), 463 (−18), 454 (−21), 440 (−11), 426 (−22), 402 (sh, 10), 367 (68), 346 (sh, 29), 317 (−68), 292 (−12), 286 (−15), 258 (107). IR (KBr): 2955*m*, 2922*m*, 2866*w*, 1741*s*, 1494*w*, 1455*m*, 1425*m*, 1378*w*, 1270*m*, 1232*s*, 1178*w*, 1161*w*, 1093*m*, 1050*w*, 1030*w*, 930*w*, 795*w*, 739*w*, 696*s*, 670*w*, 580*w*, 544*w*, 457*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.47–7.20 (*m*, 20 H); 6.07–6.00 (*m*, 4 H); 2.20–2.05 (*m*, 4 H); 2.00–1.85 (*m*, 4 H); 1.65–1.22 (*m*, 8 H); 1.02 (*t*, *J* = 7.4, 6 H); 0.96 (*t*, *J* = 7.4, 6 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 162.77 (C=O); 162.74 (C=O); 155.56; 154.88; 152.74; 152.06; 151.60; 151.18; 150.43; 149.83; 148.74; 147.39; 146.27; 146.18; 146.15; 144.80; 144.71; 144.37; 144.31; 143.40; 143.06; 142.41; 142.26; 142.07; 141.31; 141.28; 140.30 (2 ×); 139.00 (arom. C); 138.98 (arom. C); 137.79; 137.49; 135.78; 132.88; 132.62; 131.29; 131.00; 128.55 (arom. CH); 128.51 (arom. CH); 128.47 (arom. CH); 128.40 (arom. CH); 127.18 (arom. CH); 127.16 (arom. CH); 79.66 (2 Ph*C*HO); 67.11 (fullerene sp^3-C); 66.66 (fullerene sp^3-C); 38.27 (methano bridge); 37.83 (CH_2); 37.80 (CH_2); 18.87 (CH_2); 18.82 (CH_2); 13.80 (Me); 13.75 (Me); 29.65 (impurity). MALDI-TOF-MS (DHB): 1573.0 (M^-), 1398.7, 866.2, 853.2, 839.0 (C_{70}^-).

Product of HPLC fraction IV: R_f (CH_2Cl_2/hexane 1:1) 0.40. UV/VIS (CH_2Cl_2): 652 (sh, 1900), 529 (sh, 12800), 461 (19300), 434 (20000), 398 (19900), 371 (sh, 17000), 331 (sh, 24000). CD (CH_2Cl_2): 670 ($\Delta\varepsilon$ = 3), 645 (−3), 619 (3), 572 (sh, −16), 538 (−36), 486 (51), 462 (15), 454 (18), 441 (9), 426 (19), 401 (sh, −9), 368 (−57), 348 (sh, −27), 318 (64), 292 (6), 286 (13), 259 (−99). IR (KBr): 2953*m*, 2923*m*, 2867*w*, 2851*w*, 1741*s*, 1494*w*, 1454*m*, 1425*m*, 1377*w*, 1271*m*, 1233*s*, 1177*w*, 1161*w*, 1094*m*, 1050*w*, 1030*w*, 930*w*, 795*w*, 756*w*, 739*w*, 695*s*, 670*w*, 580*w*, 544*w*, 456*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.50–7.17 (*m*, 20 H); 6.06–6.00 (*m*, 4 H); 2.17–2.05 (*m*, 4 H); 2.00–1.85 (*m*, 4 H); 1.65–1.20 (*m*, 8 H); 1.00 (*t*, *J* = 7.6. 6 H); 0.97 (*t*, *J* = 7.5, 6 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 162.81 (C=O); 162.67 (C=O); 155.40; 155.01; 152.79; 152.14; 151.58; 151.12; 150.47; 149.72; 148.85; 147.37; 146.33; 146.22; 146.18; 145.02; 144.72; 144.40; 144.22; 143.37; 143.09; 142.15; 142.12; 142.04; 141.29; 141.22; 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; 128.58 (arom. *C*H); 128.53 (arom *C*H); 128.47 (arom. *C*H); 128.41 (arom. *C*H); 127.21 (arom. *C*H); 127.13 (arom. *C*H); 79.70 (Ph*C*HO); 79.65 (Ph*C*HO); 67.10 (fullerene sp^3-C); 66.64 (fullerene sp^3-C); 38.30 (methano bridge); 37.83 (CH_2); 37.80 (CH_2); 18.86 (CH_2); 18.84 (CH_2); 13.78 (Me); 13.76 (Me); 29.65 (impurity). MALDI-TOF-MS (CCA): 1574.1 (M^+), 1442.9.

Tetrakis[(S)-1-phenylbutyl] 1,2:41,58-Bis(methano)[70]fullerene-71,71,72,72-tetracarboxylate (**11**): *Product of HPLC fraction V:* R_f (CH_2Cl_2/hexane 1:1) 0.40. UV/VIS (CH_2Cl_2): 677 (sh, 1100), 478 (16500), 428 (sh, 14700), 400 (17500), 375 (weak, 15300), 363 (15600), 334 (sh, 17000), 271 (78600). CD (CH_2Cl_2): 645 ($\Delta\varepsilon$ = 8), 360 (2), 316 (−1), 293 (0), 276 (−5). IR (KBr): 2954*m*, 2921*m*, 2867*w*, 2848*w*, 1740*s*, 1494*w*, 1455*m*, 1442*m*, 1425*m*, 1415*w*, 1374*w*, 1262*s*, 1230*s*, 1221*s*, 1174*m*, 1092*m*, 1048*w*, 930*w*, 795*w*, 756*w*, 726*w*, 697*s*, 667*w*, 577*w*, 541*w*, 532*m*, 455*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.55–7.25 (*m*, 20 H); 6.14–6.08 (*m*, 2 H); 2.25–2.12 (*m*, 4 H); 2.05–1.95 (*m*, 4 H); 1.80–1.30 (*m*, 8 H); 1.08 (*t*, *J* = 7.4, 6 H); 1.04 (*t*, *J* = 7.4, 6 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 162.87 (C=O); 162.83 (C=O); 154.43; 154.25; 152.47; 152.41; 151.37; 151.35; 149.80; 149.68; 149.19; 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; 141.80; 141.49; 141.44; 141.43; 139.01 (arom. C); 138.96 (arom. C); 137.31; 137.00; 136.65; 135.20; 131.53; 131.10; 130.53; 128.57 (arom. CH); 128.55 (arom. CH); 128.48 (arom. CH); 128.41 (arom. CH); 127.22 (arom. CH); 127.14 (arom. CH); 79.71 (Ph*C*HO); 79.68 (Ph*C*HO); 66.19 (fullerene sp^3-C); 65.94 (fullerene sp^3-C); 37.85 (CH_2); 37.80 (CH_2); 36.81 (methano bridge); 18.87 (CH_2); 18.85 (CH_2); 13.80 (Me); 13.77 (Me); 29.66 (impurity). MALDI-TOF-MS (DHB): 1572.7 (M^-), 1398.2, 866.4, 853.4, 840.0 (C_{70}^-).

4. *Reaction of C_{70} Bis-adducts with Diethyl 2-Bromopropanedioate.* 4.1. *C_{70} Tetraadduct (±)-***4**. To a soln. of (±)-**2** (75.0 mg, 0.054 mmol) and **13a** (2 equiv., 25.8 mg, 0.108 mmol) in CCl_4 (50 ml) was added DBU (16.4 mg, 0.108 mmol) in CCl_4 (5 ml). After 2 d, the solvent was evaporated. CC (SiO_2 *H*, CH_2Cl_2/AcOEt 98.5:1.5) afforded

two amber fractions of (±)-**16** (together with other isomeric tris-adducts) and (±)-**4**. Recrystallization from CH_2Cl_2/cyclohexane followed by drying at 25°/10^{-1} Torr gave (±)-**16** as a mixture with other isomeric tris-adducts (13.6 mg, 16%) and (±)-**4** (35.0 mg, 38%) as black solids. *72,72,73,73-Tetraethyl 71,71,74,74-Tetrakis[(ethoxycarbonyl)methyl] 1,2:31,32:54,55:59,60-Tetrakis(methano)[70]fullerene-71,71,72,72,73,73,74,74-octacarboxylate* ((±)-**4**): R_f (CH_2Cl_2/AcOEt 98.5:1.5) 0.21. UV/VIS (CH_2Cl_2): 628 (4000), 577 (4300), 526 (8500), 488 (sh, 9400), 435 (16000), 380 (25100), 272 (sh, 130600), 259 (150300). IR (KBr): 2978*w*, 2928*w*, 2850*w*, 1744*s*, 1465*w*, 1444*w*, 1420*w*, 1380*m*, 1296*m*, 1235*s*, 1198*s*, 1096*m*, 1060*s*, 1052*m*, 1021*m*, 856*w*, 794*w*, 725*w*, 703*w*, 650*w*, 582*w*, 556*w*, 532*w*, 513*w*, 479*w*, 457*w*, 425*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.99 (*d*(*A*), J_{AB} = 15.6, 2 H); 4.95 (*d*(*A'*), $J_{A'B'}$ = 15.3, 2 H); 4.90 (*d*(*B'*), $J_{A'B'}$ = 15.3, 2 H); 4.86 (*d*(*B*), J_{AB} = 15.6, 2 H); 4.57 (*q*, *J* = 7.1, 4 H); 4.35–4.18 (*m*, 12 H); 1.49 (*t*, *J* = 7.1, 6 H); 1.32 (*t*, *J* = 7.3, 6 H); 1.28 (*t*, *J* = 7.3, 6 H); 1.22 (*t*, *J* = 7.1, 6 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 166.45 (C=O); 166.41 (C=O); 164.22 (C=O); 163.93 (C=O); 162.50 (C=O); 162.42 (C=O); 156.54; 152.13; 151.92; 149.41; 146.72; 146.58; 146.37; 145.98; 145.37; 144.36; 144.18; 143.75; 143.65; 143.41; 143.32; 142.16; 142.02; 141.79; 141.18; 140.37; 139.43; 138.66; 137.54; 137.33; 136.33; 134.88; 134.61; 133.63; 133.00; 129.94; 128.69; 69.03 (fullerene sp^3-C); 67.61 (fullerene sp^3-C); 64.58 (fullerene sp^3-C); 64.09 (fullerene sp^3-C); 63.29 (CH_2); 62.85 (CH_2); 62.74 (CH_2); 62.71 (CH_2); 61.77 (CH_2); 61.73 (CH_2); 40.95 (methano bridge); 39.23 (methano bridge); 14.22 (Me); 14.20 (Me); 14.17 (Me); 13.94 (Me). MALDI-TOF-MS (CCA): 1705.0 (M^+), 1661.2 ([$M - C_2H_4O$]$^+$), 1603.5.

4.2. *C_{70} Tris-adduct* **5** *and Tetrakis-adduct* **6**. As described for (±)-**4**, with **3** (35.0 mg, 0.025 mmol), **13a** (1 equiv., 6.0 mg, 0.025 mmol), CCl_4 (30 ml), DBU (3.8 mg, 0.025 mmol), and CCl_4 (5 ml; 3 d). CC (SiO_2 *H*, CH_2Cl_2/AcOEt 98.5:1.5) afforded two amber fractions of **5** and **6**. Recrystallization from CH_2Cl_2/cyclohexane followed by drying at 25°/10^{-1} Torr gave **5** (4.4 mg, 11%) with very small amounts of impurities and **6** (7.9 mg, 18%) as black solids.

72,72-Diethyl 71,71,73,73-Tetrakis[(ethoxycarbonyl)methyl] 1,2:31,32:41,58-Tris(methano)[70]fullerene-71,71,72,72,73,73-hexacarboxylate (**5**): R_f (CH_2Cl_2) 0.18. UV/VIS (CH_2Cl_2): 683 (sh, 600), 642 (sh, 2500), 508 (sh, 9200), 458 (15200), 382 (sh, 17100), 364 (17800), 262 (sh, 85500). IR (KBr): 2977*w*, 2927*w*, 2850*w*, 1746*s*, 1464*w*, 1440*w*, 1421*w*, 1377*w*, 1294*m*, 1246*m*, 1198*s*, 1179*m*, 1096*m*, 1060*w*, 1023*m*, 858*w*, 794*w*, 758*w*, 723*w*, 660*w*, 579*w*, 543*w*, 523*w*, 456*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 4.98 (*s*, 4 H); 4.95 (*d*(*A*), J_{AB} = 15.7, 2 H); 4.89 (*d*(*B*), J_{AB} = 15.7, 2 H); 4.54 (*q*, *J* = 7.1, 4 H); 4.31 (*q*, *J* = 7.1, 4 H); 4.27 (*q*, *J* = 7.2, 4 H); 1.48 (*t*, *J* = 7.1, 3 H); 1.33 (*t*, *J* = 7.2, 6 H); 1.30 (*t*, *J* = 7.2, 6 H); 1.25 (*t*, *J* = 7.1, 3 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 166.42 (C=O); 166.37 (C=O); 163.98 (C=O); 162.64 (C=O); 162.46 (C=O); 155.22; 153.49; 153.27; 152.65; 151.65; 149.93; 149.72; 149.06; 148.75; 148.26; 147.30; 147.27; 143.49; 143.14; 143.08; 142.88; 142.80; 142.18; 142.07; 141.78; 141.68; 141.66; 141.17; 140.78; 137.70; 136.69; 136.61; 136.33; 132.53; 132.35; 131.96; 127.61; 67.21 (fullerene sp^3-C); 66.20 (fullerene sp^3-C); 66.07 (fullerene sp^3-C); 65.85 (fullerene sp^3-C); 63.85; 63.28; 62.91; 62.77 (CH_2); 62.70 (CH_2); 61.82 (CH_2); 61.75 (CH_2); 40.81 (methano bridge); 36.74 (methano bridge); 36.57 (methano bridge); 14.20 (Me); 14.15 (Me); 13.97 (Me). MALDI-TOF-MS (CCA): 1574.6, 1546.3 ([M – H]$^+$), 1502.8 (M – EtO]$^+$).

71,71,73,73-Tetraethyl 72,72,74,74-Tetrakis[(ethoxycarbonyl)methyl] 1,2:31,32:41,58:65,66-Tetrakis(methano)[70]fullerene-71,71,72,72,73,73,74,74-octacarboxylate (**6**): R_f (CH_2Cl_2) 0.10. UV/VIS (CH_2Cl_2): 691 (sh, 700), 617 (4200), 492 (10600), 444 (14400), 393 (sh, 16200), 361 (20200), 289 (sh, 72900), 258 (107000). IR (KBr): 2978*w*, 2922*w*, 2850*w*, 1746*s*, 1465*w*, 1443*w*, 1421*m*, 1379*m*, 1297*m*, 1278*m*, 1250*s*, 1198*s*, 1180*s*, 1094*m*, 1022*m*, 939*w*, 858*w*, 794*w*, 756*w*, 731*w*, 708*w*, 688*w*, 660*w*, 582*w*, 539*w*, 525*w*, 503*w*, 458*w*, 428*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 4.97 (*d*(*A*), J_{AB} = 15.7, 4 H); 4.89 (*d*(*B*), J_{AB} = 15.7, 4 H); 4.52 (*q*, *J* = 7.2, 4 H); 4.28 (*q*, *J* = 7.2, 8 H); 4.19 (*q*, *J* = 7.1, 4 H); 1.45 (*t*, *J* = 7.2, 6 H); 1.31 (*t*, *J* = 7.1, 12 H); 1.20 (*t*, *J* = 7.1, 6 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 166.44 (C=O); 164.30 (C=O); 163.52 (C=O); 162.54 (C=O); 153.64; 153.57; 148.64; 148.20; 147.53; 143.56; 143.34; 142.45; 142.12; 141.72; 141.09; 137.91; 136.61; 136.00; 133.04; 133.00; 132.85; 124.37; 67.46 (fullerene sp^3-C); 66.33 (fullerene sp^3-C); 63.46; 63.20; 62.73 (CH_2); 62.60; 61.76 (CH_2); 40.91 (methano bridge); 37.79 (methano bridge); 14.19 (Me); 13.79 (Me). MALDI-TOF-MS (CCA): 1705.0 (M^+), 1660.7 ([$M - C_2H_4O$]$^+$), 1602.3.

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