147. Synthesis, Separation, and Characterization of Optically Pure C_{76} Mono-Adducts

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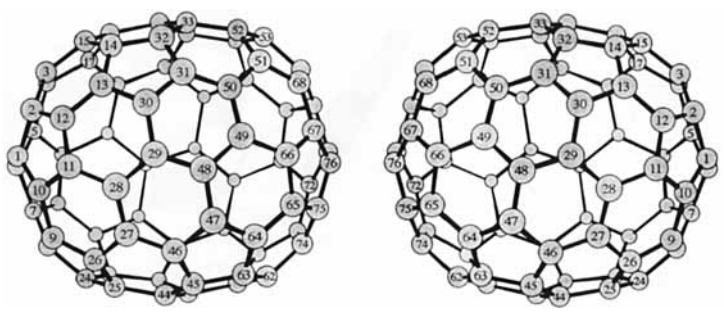
Nucleophilic *Bingel* cyclopropanation of D_2-C_{76} with bis[(*S*)-1-phenylbutyl] 2-bromomalonate in toluene in the presence of base yielded three constitutionally isomeric pairs of diastereoisomeric mono-adducts together with one other constitutional isomer. All seven mono-adducts were isolated in optically pure form by prep. HPLC on a (*S,S*)-*Whelk-O1* chiral stationary phase. They represent the first optically pure adducts of an inherently chiral fullerene. Characterization by UV/VIS, CD, ^{13}C- and ^{1}H-NMR spectroscopy allowed identification of pairs of stereoisomers and symmetry assignments: the two pairs of diastereoisomers which were isolated as the major product possess C_1 symmetry, whereas the third pair of diastereoisomers, which is a minor product, is C_2-symmetrical. The circular dichroism spectra of the optically active C_{76}-adducts showed very pronounced *Cotton* effects resulting from strong chiroptical contributions of the chiral fullerene chromophore with the maximum observed $\Delta\varepsilon$ values being twice as high than those previously measured for optically active adducts of achiral fullerenes with a chiral addition pattern. Whereas the regioselectivity of mono-additions to C_{70} correlates with the degree of local bond curvature and the regioselectivity of multiple *Bingel* cyclopropanations of C_{60} with electronic parameters such as coefficients of the *l*owest *u*noccupied *m*olecular *o*rbital (LUMO), no such simple predictive correlations exist for the nucleophilic addition to C_{76}. Despite full spectral characterization, an unambiguous structural assignment of the isolated compounds was not possible, except for the two C_2-symmetrical isomers. Based on considerations of local bond curvature and the previous experiences with the chemistry of C_{70}, the structures of the C_2-symmetrical stereoisomers were assigned as (*S,S,*^{f}*C*)-**3** and (*S,S,*^{f}*A*)-**3**, resulting from addition to the polar α-type C(1)–C(6) bond.

1. Introduction. – With the isolation and structure determination of D_2-C_{76}, the first form of chiral carbon was reported in 1991 [1] (*Fig. 1*). The described constitutional isomer of C_{76} was predicted by calculations to be the only stable form of [76]fullerene obeying the



(^{f}*A*)-C_{76} (^{f}*C*)-C_{76}

Fig. 1. *Molecular structures and numbering of* (^{f}A)- *and* (^{f}C)-D_2-C_{76}. For the stereochemical descriptors, see [11a, b]; for the numbering, see [11c].

'isolated pentagon rule' (IPR; each pentagon on the fullerene surface is surrounded by five hexagons) and having a closed electronic shell with a fully occupied *h*ighest *o*ccupied *m*olecular *o*rbital (HOMO) [2]. It is the only C_{76} isomer [1] [3] which was isolated from soot produced by the method described by *Krätschmer* and *Huffman* [4].

So far, the chemistry of C_{76} is almost unexplored due to the low abundance of this carbon sphere in fullerene soot and to its complicated chromatographic separation from the other higher fullerenes [5] [6]. The chromatographic resolution of the C_{76} enantiomers has not been achieved yet; however, *Hawkins et al.* reported a kinetic resolution on very small scale by the *Sharpless* asymmetric osmylation reaction [7a, b]. The ozonation [7c] or hydrogenation [7d] of a fullerene mixture containing C_{76} was investigated by different groups. Only a single covalent mono-adduct of C_{76} has been isolated in pure form and fully characterized [6], and an X-ray crystal structure of C_{76}, co-crystallized with six S_8 units, was described in literature [3b].

In I_h-C_{60}, all C-atoms and all 6–6 bonds (bonds between two six-membered rings) are identical and only one mono-adduct is formed in most cases by nucleophilic or cycloaddition to one of these bonds [8]. In D_2-C_{76}, however, the presence of 19 different C-atoms and 15 different 6–6 bonds gives rise to a large number of possible mono-adduct isomers. In the case of the *Diels-Alder* addition to C_{76}, we reported the formation of a minimum of six constitutional isomers, one of which, with C_1 symmetry, was isolated in pure form and fully characterized [6]. Based on ^{1}H-NMR spectroscopy and consideration of bond reactivities modulated by the local curvature of the fullerene surface, the structure of an additional isomer with C_2 symmetry was tentatively assigned.

To express different degrees of local curvature on a fullerene surface, *Haddon* and coworkers calculated the pyramidalization angles of some of the C-atoms by applying the concept of the π-*o*rbital *a*xis *v*ector (POAV) to fullerenes [9]. *Fig. 2,a* shows the

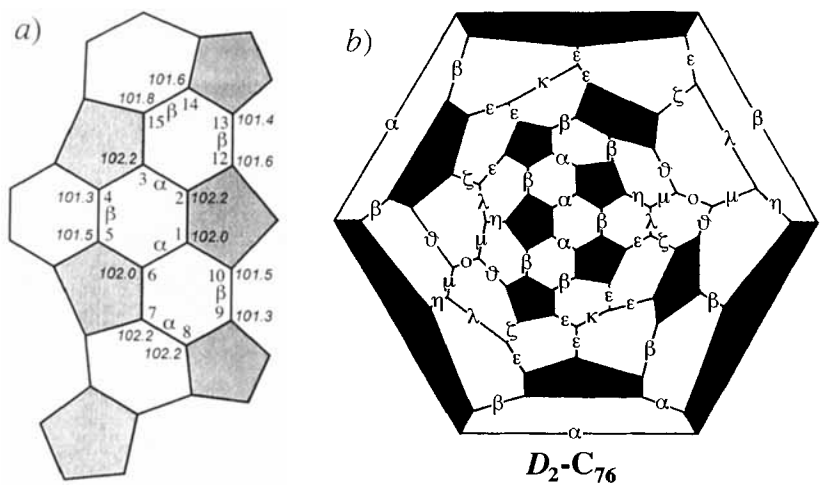


Fig. 2. a) *View on a pole of C_{76}, showing different types of 6–6 bonds* [6] *and the pyramidalization of the atoms involved, as expressed by the calculated π-orbital axis vector angles* (POAV) [7a] [9]. b) Schlegel *diagram showing the different types of 6–6 bonds with respect to their curvature* (qualitative model) [6]. The three C_2 axes of the molecule pass through the center of bonds of type α, κ, and *o*, respectively.

calculated POAV angles [7a] [9] for the atoms of the most curved bonds in the polar region of C_{76}. The higher the POAV values, the more pyramidalized the C-atoms are. In a qualitative model, we distinguished between different types of 6–6 bonds according to the number of pentagons fused to a naphthalene unit with the respective 6–6 bond at its center [6]. The most curved bonds (type α) at the poles of C_{76} are surrounded by less curved bonds of type β, and the distribution of the different bond types on the fullerene surface is shown in a *Schlegel* diagram depicted in *Fig. 2,b*. Addition to the most curved bonds of type α and β leads to five possible constitutionally isomeric mono-adducts.

The nucleophilic cyclopropanation with 2-bromomalonate derivatives in the presence of base (*Bingel* reaction) [10], when applied to C_{70}, showed a very high selectivity for addition to the most curved polar bond of type α to form only one out of the four possible mono-adducts [10] [11a]. In the case of the *Diels-Alder* reaction, however, three constitutionally isomeric mono-adducts were isolated [6]. Due to the high selectivity of the *Bingel* reaction observed with C_{70}, a lower number of mono-adducts might also be expected in the reaction of 2-bromomalonates with C_{76} compared to the *Diels-Alder* addition [6]. If mono-addition occurs only at the most curved bonds (type α), formation of two constitutional isomers could be expected. Reaction at the C(1)–C(6) bond, lying on a C_2 axis of C_{76} (*Fig. 3*, yellow), would give rise to a C_2-symmetrical mono-adduct, whereas addition at bonds C(2)–C(3) or C(7)–C(8) which are identical by symmetry (*Fig. 3*, red) would yield a C_1-symmetrical derivative.

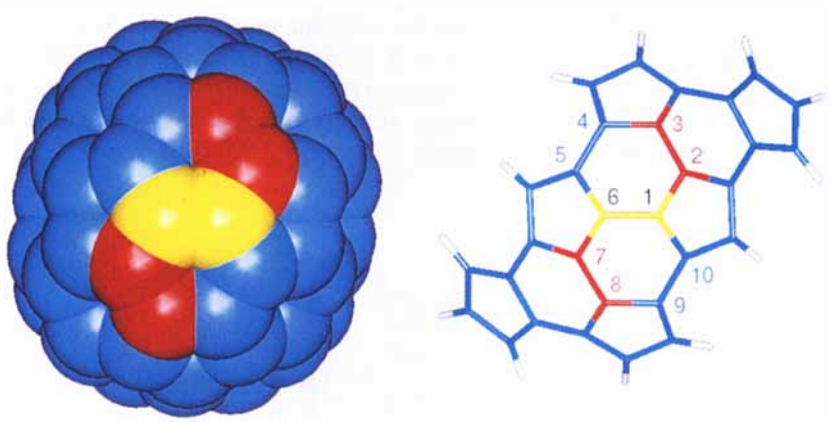


Fig. 3. *View on a pole of* C_{76} (only one enantiomer is shown). The most curved bonds (type α) are marked in color: bond C(1)–C(6) (yellow) is lying on one of the C_2 axis of C_{76}; bonds C(2)–C(3) and C(7)–C(8) (red) are identical due to the fullerene symmetry.

In this paper, we report the *Bingel* cyclopropanation of C_{76} using a chiral 2-bromomalonate derivative with defined configuration. Upon addition to different bonds of C_{76}, constitutionally isomeric pairs of diastereoisomers are formed due to the superimposition of the chirality of the addend to that of the inherently chiral fullerene. Chromatographic separation of the diastereoisomers should allow the study of the chiroptical properties of derivatives of inherently chiral fullerene chromophores, which has not been reported in literature so far.

It was shown that chiral fullerene chromophores [12], arising either from inherently chiral fullerenes [7a, b] [13] or from fullerenes with a chiral addition pattern [11a] [14], give rise to much stronger chiroptical effects than fullerene derivatives, whose chirality originates exclusively from the addends [11a] [15]. This is clearly reflected in the circular dichroism (CD) spectra.

2. Results and Discussion. – 2.1. *Functionalization of C_{76} and Isolation of the Mono-adducts.* A total of 56.2 mg of C_{76}, which was isolated by prep. HPLC [6] in two steps from soot extract enriched in higher fullerenes, was reacted with 1 equiv. of optically active bis[(*S*)-1-phenylbutyl] 2-bromomalonate (**1**) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in toluene. Column chromatography (SiO_2, gradient hexane/CH_2Cl_2 5:1 to CH_2Cl_2) allowed partial separation of the mono- from the bis-adducts and unreacted fullerene. Complete separation of the mono-adduct fraction was achieved by prep. HPLC on a *Buckyclutcher I* column [5 g] (hexane/CH_2Cl_2 7:3). To separate the isomeric mono-adducts, several stationary phases and solvent compositions were tested by anal. HPLC. The best separation, which was subsequently used for prep. HPLC (*Fig. 4*), was obtained on a chiral (*S,S*)-*Whelk-O1* column [16] (hexane/CH_2Cl_2 7:3). Five fractions (*I–V*, *Fig. 4*) were collected in a first run. The two isomers in *Fraction IV* were separated in an additional step using the same conditions. *Fraction I* still contained a small amount of another isomer and needed to be further purified. Both components of *Fraction I* (*Ia* and *Ib*) could be isolated in pure form by repetitive HPLC on the same column, using a slightly less polar solvent mixture (hexane/CH_2Cl_2 3:1). The following quantities of pure mono-adduct isomers were isolated from the different fractions: *Fraction Ia*, 9.1 mg (11%); *Fraction Ib*, 1.5 mg (2%); *Fraction II*, 10.6 mg (13%); *Fraction III*, 12.5 mg (16%); *Fraction IVa*, 0.6 mg (< 1%); *Fraction IVb*, 1.4 mg (2%); *Fraction V*, 13.9 mg (18%). Another small fraction containing at least two isomers was eluted before *Fraction I*, and was not further investigated.

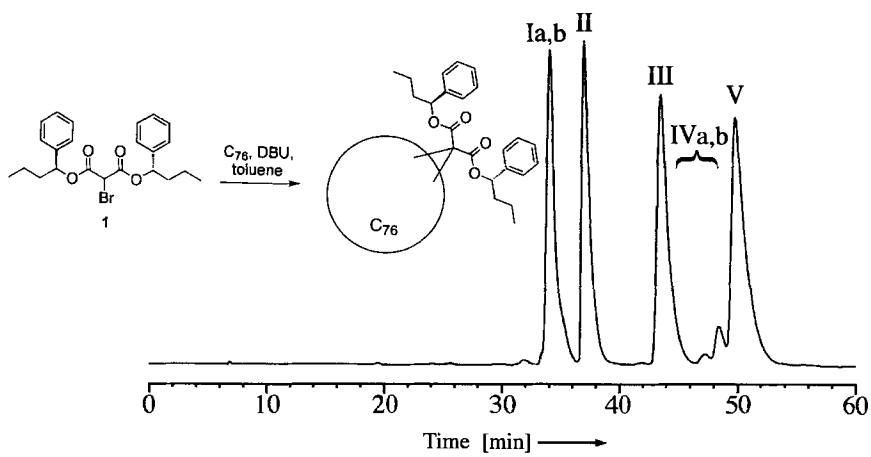


Fig. 4. *HPLC of the separation of the optically active C_{76} mono-adducts obtained by reacting the fullerene with* **1** *in the presence of base.* Conditions: (*S,S*)-*Whelk-O1* (*Regis*), hexane/CH_2Cl_2 7:3, flow rate 2 ml/min, detection at λ 310 nm.

2.2. *Spectroscopic Characterization of the Mono-adducts.* The IR spectra of the different mono-adducts are very similar even in their fine structure and, therefore, did not allow a distinction between the various isomers formed. The electronic absorption spectra of the isolated products are shown in *Fig. 5*. The onset of absorption is located around λ 900 nm, and characteristic bands around λ 400 and 570 nm, as well as a broad maximum around λ 700 nm were observed for all compounds. The fact that the spectra of the products of *Fractions Ia* and *III*, *Fractions II* and *V*, as well as of *Fractions Ib* and *IVb* (*Figs. 5,a–c*) are almost identical pairwise, suggests that the corresponding adduct pairs have the same constitution. Significant differences exist, however, between the spectra of constitutional isomers, and this is also reflected by their colors in solution. CH_2Cl_2

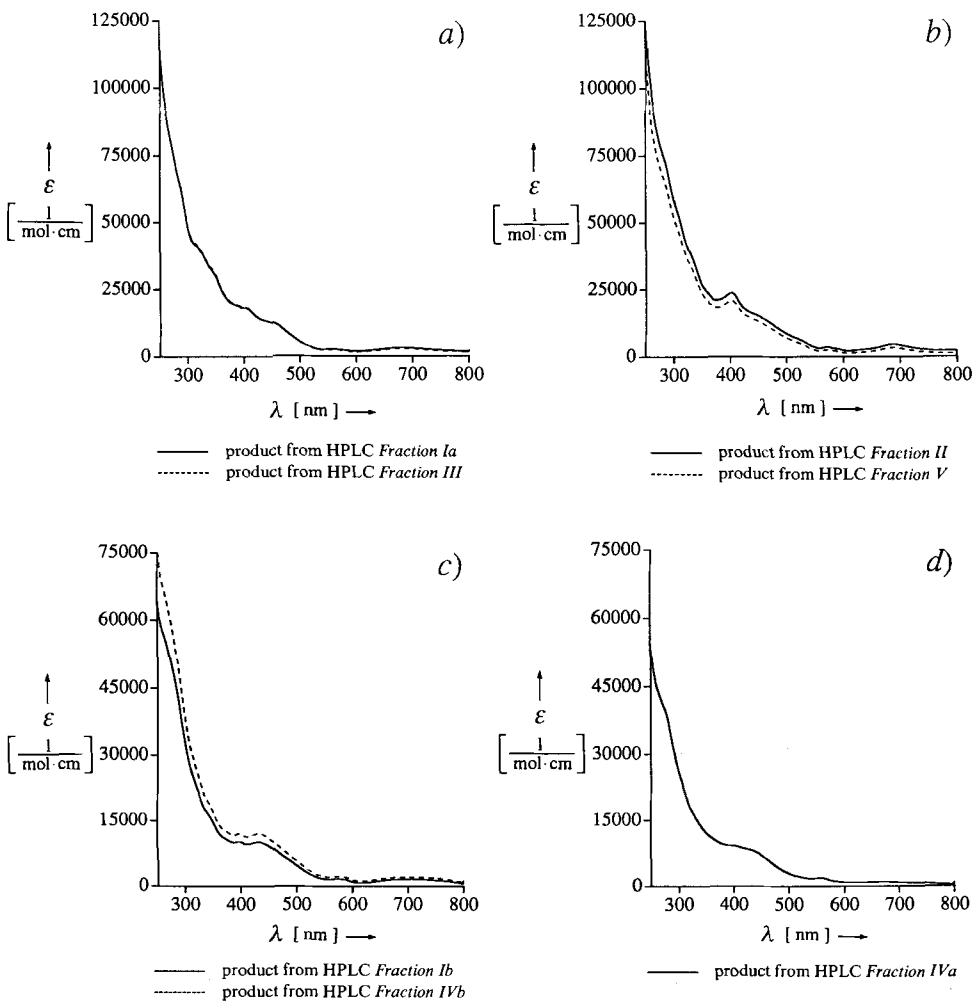


Fig. 5. *UV/VIS Spectra* (CH_2Cl_2) *of the pure diastereoisomers of identical constitution contained in* a) Fractions Ia *and* III, b) Fractions II *and* V, c) Fractions Ib *and* IVb, *and* d) Fraction IVa

solutions of HPLC *Fractions Ia*, *Ib*, *III*, and *IVb* are greenish yellow, those of *Fractions II* and *V* are brownish yellow, and *Fraction IVa* is yellow. The UV/VIS spectra of the two major constitutional isomers together with the spectrum of the previously described *Diels-Alder* adduct **2** [6] are superimposed in *Fig. 6*. The similarity between the latter spectrum and those arising from HPLC *Fractions Ia* and *III* strongly suggests that the three compounds are products arising from reaction at the same 6–6 bond. It is noteworthy that the major isomers isolated from *Fractions Ia*, *II*, *III*, and *V* have significantly stronger absorptions than the minor products obtained from *Fractions Ib*, *IVa*, and *IVb*.

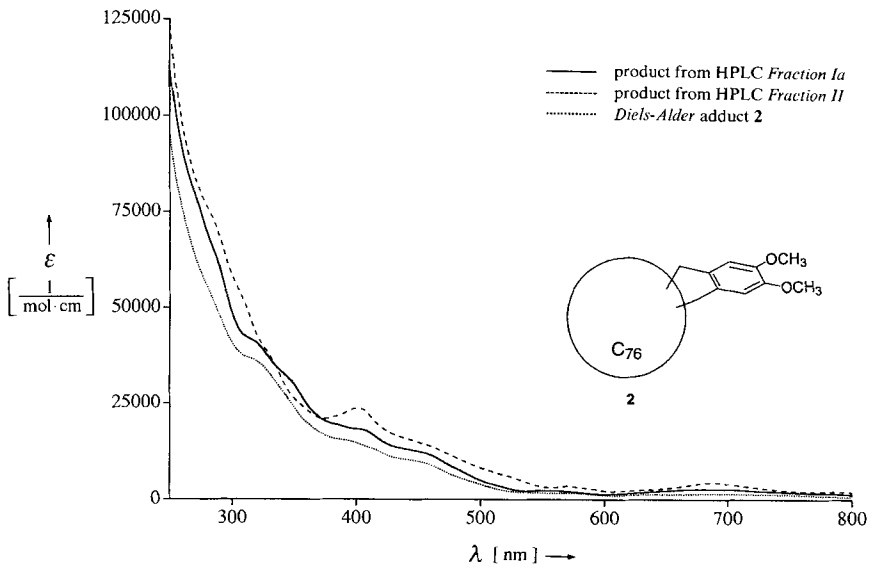


Fig. 6. *UV/VIS Spectra* (CH_2Cl_2) *of the pure diastereoisomers contained in* Fractions Ia *and* II *in comparison to the spectrum of the previously reported* Diels-Alder *adduct* **2** [6]

The compounds obtained from *Fractions Ia* and *III*, *Ib* and *IVb*, as well as from *Fractions II* and *V* form three constitutionally isomeric pairs of diastereoisomers, which is nicely reflected by their circular dichroism (CD) spectra (*Fig. 7*). The CD spectra show strong *Cotton* effects due to the chiroptical contributions of the inherently chiral fullerene chromophore. Since the contributions from the chiral addend are small, the CD curves of the diastereoisomer couples display mirror image shapes, as was previously observed for C_{70} adducts with chiral addition patterns [11a]. The products in *Fractions Ia*, *Ib*, *IVa* (CD spectrum not shown), and *V* should be adducts of the same C_{76} enantiomer, as their CD spectra show positive values between λ 250 and 320 nm, negative values between λ 320 and 490 nm, and again positive values above λ 500 nm. The CD spectra shown in *Fig. 7* are the first ones recorded for adducts of an inherently chiral fullerene. The maximum $\Delta\varepsilon$ values measured are approximately twice as large as those observed for optically pure derivatives of inherently achiral fullerenes with a chiral addition pattern [11a].

The symmetry of the obtained mono-adduct isomers was determined by their ^{1}H- and ^{13}C-NMR spectra. The ^{13}C-NMR spectra too reflected nicely the presence of constitution-

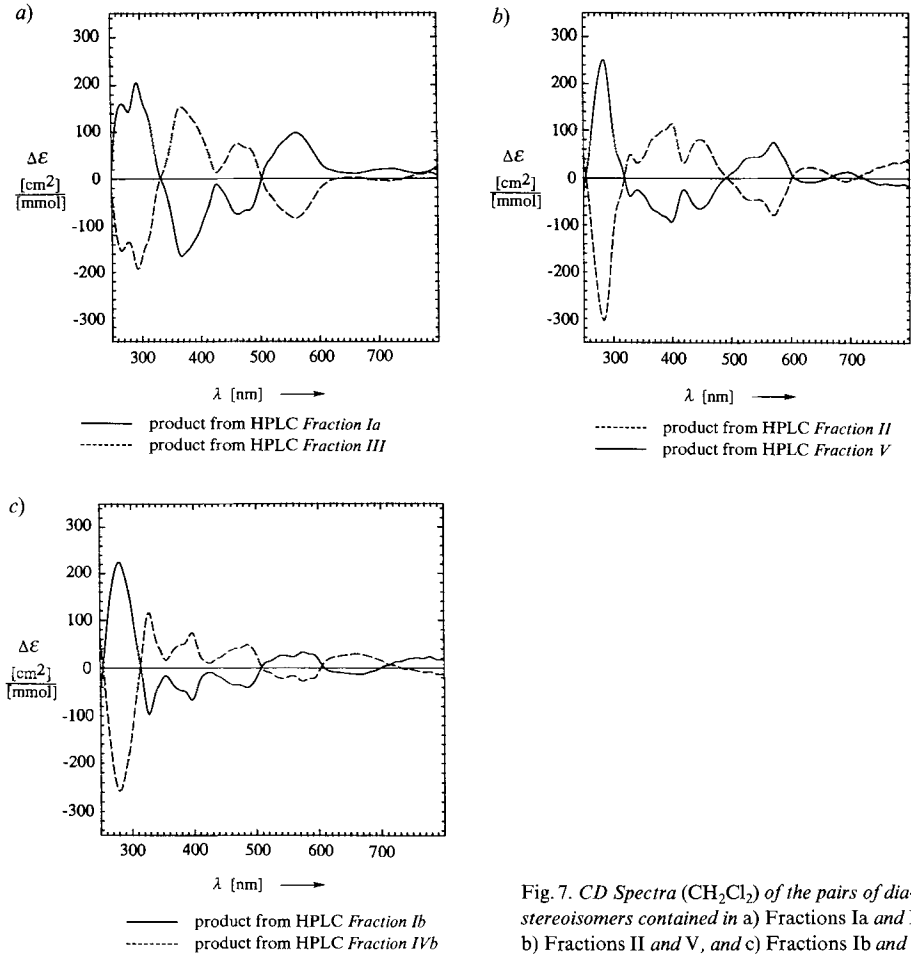


Fig. 7. *CD Spectra* (CH_2Cl_2) *of the pairs of diastereoisomers contained in* a) Fractions Ia *and* III, b) Fractions II *and* V, *and* c) Fractions Ib *and* IVb

ally isomeric pairs of diastereoisomers, displaying similar line patterns for the products of *Fractions Ia* and *III*, or *II* and *V*, respectively (*Fig. 8*). For a C_1-symmetrical adduct, a total of 74 signals for fullerene sp^2-C-atoms, eight signals for the Ph-C-atoms (2 around 140 ppm and 6 around 128 ppm), and two signals around 160 ppm for the two C=O groups are expected. The spectra of the four products from *Fractions Ia*, *II*, *III*, and *V* all showed two signals for the fullerene sp^3-C-atoms between 74 and 64 ppm, a total of four lines for the CH_2 and two lines for the Me groups, and they displayed more than 79 signals in the region between 165 and 125 ppm, thus revealing C_1 symmetry for the isolated compounds. The quantities of the minor products obtained from *Fractions Ib* and *IVb* were not sufficient to record ^{13}C-NMR spectra.

The main difference between the constitutional isomers was seen in their ^{1}H-NMR spectra. In the spectra of the products from HPLC *Fractions Ia* and *III*, *II* and *V*, as well as *IVa*, the protons at the stereogenic centers in the ester side chains appeared as two distinct *t* of equal intensity around 6 ppm, and two *t* of equal intensity were also observed

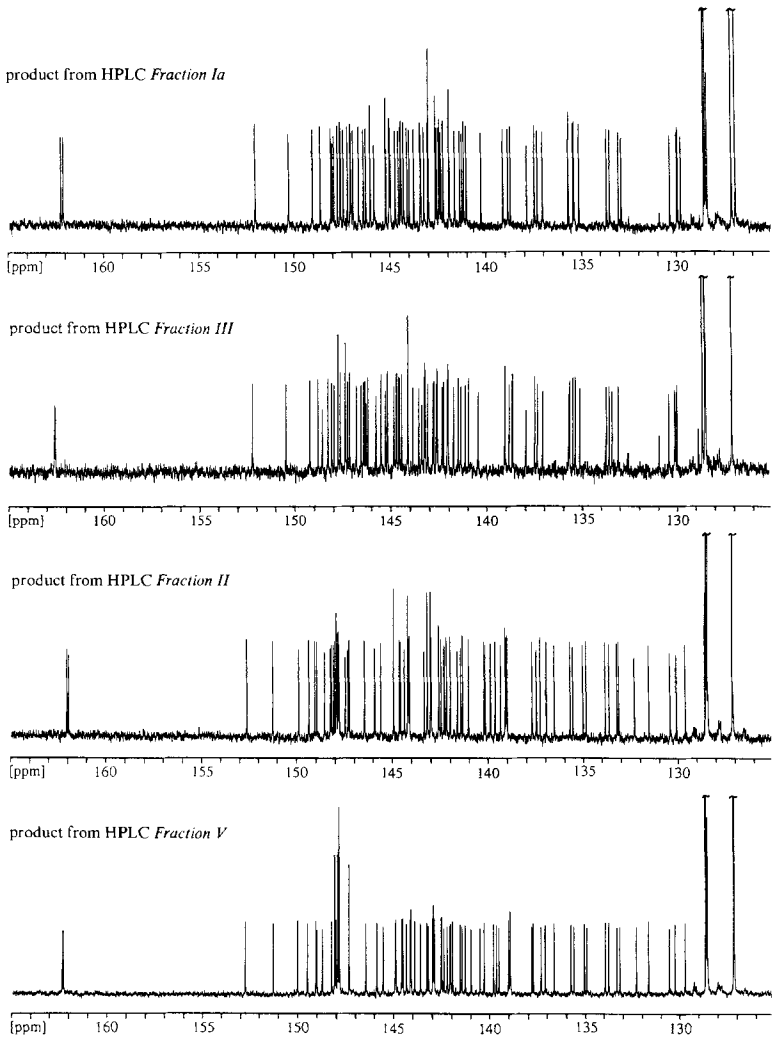


Fig. 8. *Expansion of the aromatic region of the* ^{13}C*-NMR spectra* (125.8 MHz, $CDCl_3$) *of the four isomeric* C_{76} *mono-adducts isolated from HPLC* Fractions Ia, II, III, *and* V

for the Me protons. These data further support the C_1 symmetry assigned to these compounds on the basis of the ^{13}C-NMR spectra. In the spectra of the minor products in *Fractions Ib* and *IVb*, one distinct *t* integrating for 2 H appeared around 6 ppm for the protons at the stereogenic centers in the ester side chains, and one *t* with an integration corresponding to 6 H was observed for the Me groups. Thus, the ^1H-NMR data strongly support the presence of two C_2-symmetrical stereoisomers.

The analysis of the ^1H-NMR spectra of the minor isomers from *Fractions Ib*, *IVa*, and *IVb* was complicated by the presence of small amounts of non-fullerenic impurities and the fact that, even after prolonged drying at *ca.* 10^{-7} Torr (room temp.), hexane could not

be completely removed. The missing diastereoisomer of *IVa* may be one of the two compounds contained in the very small mono-adduct fraction that was eluted before *Fraction I*; however, this was not further investigated.

2.3. *Discussion of the Structural Assignments.* A total of 15 constitutional isomers can theoretically be formed by mono-addition of **1** to any of the 6–6 bonds in C_{76}. Twelve of them have C_1 and three C_2 symmetry. A C_2-symmetrical isomer is formed when the addition occurs across one of the 6–6 bonds lying on one of the three C_2 axis of the D_2-symmetrical fullerene. Based on the results obtained previously with C_{70} [6] [11a], we expected mono-addition to occur predominantly at the most curved bonds of type α, with formation of the two constitutionally isomeric pairs of diastereoisomers **3** and **4**, shown in *Fig. 9*. The diastereoisomers **3** resulting from addition at the α-type bond C(1)–C(6) are C_2-symmetrical, whereas functionalization at the identical α-type bonds C(2)–C(3) and C(7)–C(8) yields a pair of C_1-symmetrical diastereoisomers (**4**). Making the assumption, again based on the previous experiences with C_{70}, that the most curved bonds C(2)–C(3) and C(7)–C(8) (*Fig. 2,a*) react preferentially, we initially expected a product distribution **4**/**3** which is larger than the statistical 2:1 ratio obtained at identical reactivity of the two different α-type bonds. The experimental data clearly show that these predictions of the regioselectivity were incorrect.

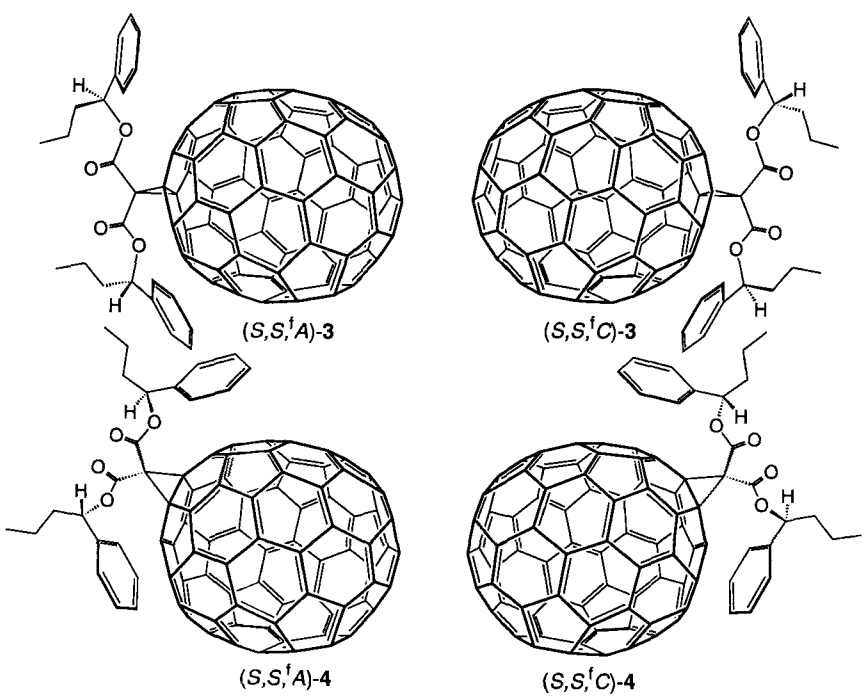


Fig. 9. *Pairs of diastereoisomeric mono-adducts arising from addition to α-type bonds.* Top: C_2-symmetrical 1,6-adducts **3**; bottom; C_1-symmetrical 2,3-adducts **4**.

The differences in the pyramidalization of the atoms in the α- and β-type bonds around the poles of C_{76} and C_{70}, as expressed by the calculated π-orbital axis vector (POAV) angles [7a] [9], are very similar. The POAV values for the atoms at the more curved α-type bonds in C_{76} are 102.2 (C(2)–C(3)) and 102.0° (C(1)–C(6)), whereas the values for the atoms at the less curved β-type bonds are 101.6 and 101.8° (C(14)–C(15)), 101.6 and 101.4° (C(12)–C(13)), and 101.3 and 101.5° (C(4)–C(5)) (*Fig. 2,a*). In C_{70}, the POAV values for the atoms at the α-type bonds are 102.0 and 101.9°, and 101.5° for those of β-type bonds [9] [17]. *Diels-Alder* addition to C_{70} occurs predominantly at the most curved α-type bonds [6], and *Bingel* mono- as well as bis-addition even takes place exclusively at these bonds [10] [11a]. Thus, the regioselectivity of additions to C_{70} can be correctly predicted taking local curvature into account only. Apparently this is not possible in the case of C_{76}. As mentioned above, *Bingel* addition to the two α-type bonds should have yielded one C_1-symmetrical (**4**) and one C_2-symmetrical (**3**) mono-adduct as the major constitutional isomers in a ratio of $\geq 2:1$. However, two constitutional isomers with C_1-symmetry were isolated and characterized in comparable amounts as the major products. Therefore, it is not possible to predict the regioselectivity of additions to C_{76}, and possibly to other higher fullerenes, by taking local curvature into account only. Also, calculations using the electronic part of the molecular electrostatic potential as a measure for the reactivity of a fullerene double bond towards a nucleophile predict the α-type bonds to be more reactive [18]. Again, these calculations, which also take into account the difference in curvature of the double bonds, do not reflect our experimental findings. Obviously, C_{76} mono-adducts from functionalization at less curved bonds must also have been formed. Isomers **5**–**7** (*Fig. 10*), formed by addition across the β-type bonds C(4)–C(5) (**5**), C(14)–C(15) (**6**), and C(12)–C(13) (**7**) must, therefore, be taken into account as possible structures for the major products formed in the *Bingel* addition of **1** to C_{76}.

Consideration of the coefficients of the *l*owest *u*noccupied *m*olecular *o*rbital (LUMO), to which electron density is transferred from the incoming nucleophile, may be another possibility to predict the regioselectivity of the addition to higher fullerenes. Based on these, as well as on steric considerations, *Hirsch* and coworkers had explained the regioselectivity seen in multiple *Bingel* cyclopropanations of C_{60} [19]. PM3 (parametric method 3) calculations [20] showed that the largest LUMO coefficients in C_{76} are located on atoms around the equator of the molecule and that the coefficients at C(1) and C(6) in the LUMO and LUMO + 1 are almost zero [21]. Therefore, the C_2-symmetrical adduct could in principle have been formed by attack at one of the 6–6 bonds lying on the C_2-axes at the flatter equator of C_{76}. This, however, is very unikely because the bonds in question are in the center of pyrene substructures, and because, in the case of C_{70}, no evidence for a nucleophilic attack at this kind of equatorial bond has been obtained.

Although all four major product fractions could be spectroscopically characterized, an unambiguous structural assignment was not possible, and theoretical models based either on local curvature or on LUMO coefficients are unable to explain the experimental results. Even under the assumption that, similarly to C_{70}, addition must take place close to the poles of the fullerene, there are several possible constitutional isomers with C_1 symmetry. Based on the data obtained in the functionalization of C_{70}, where mono-addition selectively occurs at the most curved α-type bonds near the pole of the fullerene, one of the major constitutional isomers of C_{76} is expected to be the 2,3-adduct **4** (*Fig. 9*). The

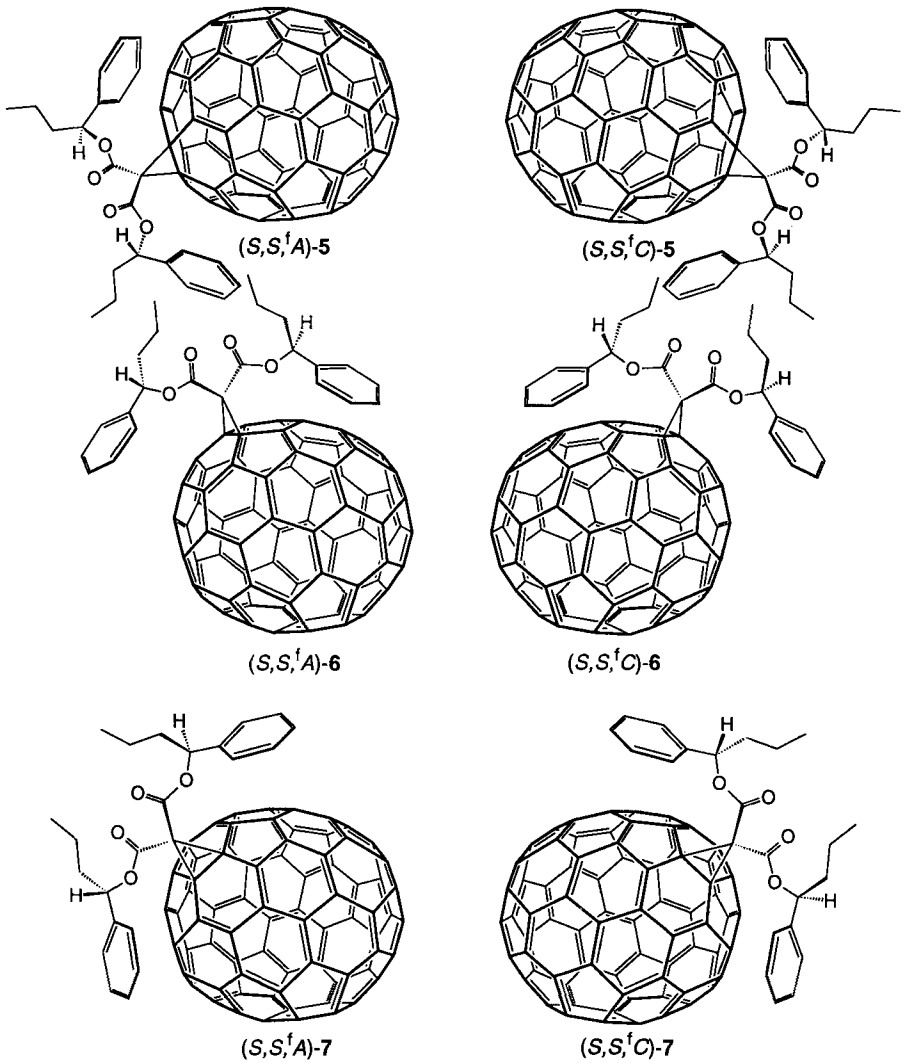


Fig. 10. *Pairs of diastereoisomeric mono-adducts arising from addition to β-type bonds.* Top: C_1-symmetrical 4,5-adducts **5**; *middle:* C_1-symmetrical 14,15-adducts **6**; bottom; C_1-symmetrical 12,13-adducts **7**.

structures of the C_2-symmetrical mono-adducts contained in *Fractions Ib* and *IVb*, on the other hand, can be assigned with good confidence as (*S*,*S*,^{f}*C*)- or (*S*,*S*,^{f}*A*)-**3**. A summary of the obtained compounds, reflecting their symmetry and their possible structural assignments, is given in the *Table*.

3. Conclusions. – Nucleophilic cyclopropanation of C_{76} using an optically active 2-bromomalonate derivative in the presence of base (*Bingel* reaction) yielded three constitutionally isomeric pairs of diastereoisomeric mono-adducts, together with one other constitutionally isomeric mono-adduct. All seven mono-adducts were obtained in

Table. *Summary of the Products Obtained from HPLC* Fractions I–V. For all compounds, yields, symmetries as observed by NMR spectroscopy, and structural assignments (where possible) are given.

HPLC *Fraction*	Yield [%]	Symmetry	Possible structures
Ia[a])	11	C_1	**4–7**
Ib[b])	2	C_2	**3**
II[c])	13	C_1	**4–7**
III[a])	16	C_1	**4–7**
IVa	< 1	C_1	**4–7**
IVb[b])	2	C_2	**3**
V[c])	18	C_1	**4–7**

[a])[b])[c]) Constitutionally isomeric pairs of diastereoisomers.

optically pure state by prep. HPLC on a chiral stationary phase. The UV/VIS, CD, and ^{13}C-NMR spectra of the mono-adducts showed distinct similarities for isomers having the same constitution which allowed facile identification of pairs of stereoisomers. The two pairs of diastereoisomers which were isolated as major products are C_1-symmetrical whereas the third pair of diastereoisomers, which is a minor product, is C_2-symmetrical. The isolated compounds represent the first optically pure adducts of an inherently chiral fullerene, and their CD spectra show very pronounced *Cotton* effects due to the strong chiroptical contributions of the chiral fullerene chromophore. The maximum $\Delta\varepsilon$ values observed are twice as high as those measured for optically active adducts of achiral fullerenes with chiral addition patterns [11a].

Despite full characterization by ^{1}H- and ^{13}C-NMR as well as by UV/VIS, IR, and CD spectroscopy, an unambiguous structural assignment of the isolated compounds was not possible, with the exception of the two C_2-symmetrical isomers. Based on considerations of bond reactivities modulated by local curvature and previous experiences with C_{70}, the structures of the C_2-symmetrical stereoisomers were assigned as (*S,S,*^{r}*C*)- and (*S,S*^{r}*A*)-**3**, resulting from addition to the polar α-type C(1)–C(6) bond. The regioselectivity of additions to C_{76}, and possibly to the other higher fullerenes, cannot be predicted based on sole consideration of either local curvature or electronic factors such as the magnitude of LUMO coefficients. This is in contrast to the regioselectivity of nucleophilic additions to C_{70}, which could be correctly predicted based on the exclusive consideration of differences in local curvature [6] [11a], or the regioselectivity of multiple *Bingel* cyclopropanations of C_{60}, which correlates with LUMO coefficients [19]. Therefore, the present study underlines the importance of exploring in more detail the covalent chemistry of the higher fullerenes which, as clearly illustrated here for C_{76}, differs significantly [22] from the known chemistry of C_{60} and C_{70}.

Experimental Part

General. Reagents used were reagent-grade commercials. HPLC solvents were from *Biosolve*, *Fluka*, *BDH*, and *Merck*. Soot extract enriched in higher fullerenes was from *Hoechst AG*, Frankfurt am Main, Germany. The percentages of the individual fullerenes in the mixture were determined from the integrated HPLC peak areas in a separation on a reversed-phase C_{18} column with optical detection at λ 310, 350, and 400 nm and corrected for the difference of UV/VIS absorption at the corresponding wavelengths (in mass-%): C_{60} 9.1%, C_{70} 22.2%, C_{76} 20.6%, C_{78} 11.7%, C_{84} 36.4%. Toluene used for the reactions was dried over molecular sieves (4 Å). TLC: *Polygram SIL*

G/UV$_{254}$ from *Macherey-Nagel*. Column chromatography: Silica gel *60* (0.040–0.063 mm) from *Fluka*. HPLC: columns: *Vydac 201TP54 RP-C$_{18}$* (5 μm), 250 mm × 4.6 mm i.d.; *Macherey-Nagel Nucleosil 100-7* silica gel (7 μm), 250 mm × 4 mm i.d.; *Regis Buckyclutcher I Trident-Tri-DNP* (5 μm), 250 mm × 4.6 mm i.d. and (10 μm) 500 mm × 21.1 mm i.d.; *Regis (S,S)-Whelk-O1* (5 μm) 250 × 4.6 mm i.d. and (5 μm) 250 mm × 10.0 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; *Variable Wavelength Monitor* UV/VIS detector from *Knauer*; all chromatograms were taken at r.t. with the detector wavelength fixed at λ 310 nm; anal. HPLC at a flow rate of 1 ml/min, injection volume 20 μl of a CH_2Cl_2/hexane soln. with different concentrations. M.p.: All fullerene derivatives decompose above 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 were measured in the 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) was used as matrix.

Bis[(S)-1-phenylbutyl] 2-bromomalonate (**1**) was synthesized according to [11a].

Purification of C_{76}. C_{76} used for the reaction was purified by HPLC as reported previously [6], with an increase of the flow rate in the first purification step to 14 ml/min.

Reaction of C_{76} with **1**. C_{76} (0.056 g, 0.062 mmol) was dissolved in dry toluene (120 ml). The soln. was sonicated and purged with Ar, after which bis[(*S*)-1-phenylbutyl] 2-bromomalonate (0.028 g, 0.062 mmol) in toluene (5 ml) and DBU (0.009 g, 0.062 mmol) in toluene (2 ml) were added. The soln. was stirred overnight at r.t. The solvent was evaporated and the mixture, dissolved in CH_2Cl_2, was chromatographed (SiO_2, hexane/CH_2Cl_2 5:1→1:1→CH_2Cl_2) to give a fraction containing mainly mono-adducts and a fraction of bis-adducts as black solids. The mono-adduct fraction was dissolved in hexane/CH_2Cl_2 1:1 (50 ml), and 1 ml was injected per run onto the prep. *Buckyclutcher I* HPLC column. Elution with hexane/CH_2Cl_2 7:3 at a flow rate of 14 ml/min gave the pure mono-adducts as a mixture which was separated by semiprep. HPLC on a *(S,S)-Whelk-O1* column. For this purpose, the mixture was dissolved in hexane/CH_2Cl_2 1:1 (20 ml) and an average of 200 μl was injected per run and eluted with hexane/CH_2Cl_2 7:3 at a flow rate of 2 ml/min. Five fractions (*I–V*) were collected. *Fraction IV* (2.7 mg) was separated in an additional step using the same conditions. *Fraction I* still contained two compounds and was redissolved in hexane/CH_2Cl_2 1:1 and reinjected onto the *(S,S)-Whelk-O1* column, using hexane/CH_2Cl_2 3:1 as the eluent, until both isomers were isolated in pure state. *Fractions Ia* (9.1 mg, 11%), *Ib* (1.5 mg, 2%), *II* (10.6 mg, 13%), *III* (12.5 mg, 16%), *IVa* (0.6 mg, <1%), *IVb* (1.4 mg, 2%), and *V* (13.9 mg, 18%) were isolated and characterized. Drying of the samples at *ca.* 10^{-7} Torr (r.t.) did not remove small amounts of hexane, which could be identified by NMR spectroscopy even after prolonged drying.

Product of HPLC *Fraction Ia*: R_f (CH_2Cl_2/hexane 1:1): 0.48. UV/VIS (CH_2Cl_2): 684 (2800), 556 (2400), 457 (sh, 11900), 402 (sh, 18200), 345 (sh, 31900), 319 (sh, 41000), 291 (sh, 59300). CD (CH_2Cl_2): 766 ($\Delta\varepsilon$ = 11), 724 (22), 661 (11), 561 (99), 480 (−68), 464 (−76), 428 (−12), 368 (−165), 315 (sh, 120), 293 (205), 279 (144), 268 (160). IR (KBr): 2952*m*, 2921*m*, 2851*m*, 1740*s*, 1509*w*, 1494*w*, 1454*m*, 1439*m*, 1394*w*, 1377*w*, 1260*m*, 1227*s*, 1201*m*, 1166*w*, 1135*w*, 1100*w*, 1078*m*, 1052*m*, 1032*w*, 929*w*, 804*m*, 790*w*, 757*m*, 740*w*, 727*w*, 695*s*, 670*w*, 643*m*, 571*s*, 553*w*, 489*w*, 445*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.40–7.18 (*m*, 10 H); 6.02 (*t*, *J* = 7.1, 1 H); 5.85 (*t*, *J* = 7.1, 1 H); 2.12–2.02 (*m*, 1 H); 1.99–1.84 (*m*, 2 H); 1.82–1.72 (*m*, 1 H); 1.52–1.42 (*m*, 1 H); 1.41–1.31 (*m*, 2 H); 1.30–1.20 (*m*, 1 H); 0.97 (*t*, *J* = 7.4, 3 H); 0.89 (*t*, *J* = 7.4, 3 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 162.28 (C=O); 162.15 (C=O); 152.09; 150.34; 149.10; 148.68; 148.15; 148.07; 147.99; 147.79; 147.66; 147.63; 147.49; 147.28; 147.14; 147.10; 147.00; 146.70; 146.44; 146.31; 146.07; 145.89; 145.26; 145.25; 145.08; 145.05; 145.01; 144.75; 144.59; 144.49; 144.45; 144.32; 144.13; 144.01; 143.77; 143.44; 143.41; 143.25; 143.03; 143.01 (2 ×); 142.64; 142.57; 142.46; 142.41; 142.34; 142.24; 141.96; 141.93; 141.64; 141.37; 141.25; 141.16; 141.03; 140.24; 139.06; 138.80; 138.67; 137.80; 137.38; 137.25; 136.95; 135.61; 135.60; 135.36; 135.30; 135.04; 133.61; 133.46; 132.98; 132.82; 130.33; 129.98; 129.91; 129.75; 128.54 (arom. CH); 128.45 (arom. CH); 128.37 (arom. CH); 127.12 (arom. CH); 126.91 (arom. CH); 79.75 (Ph*C*HO); 79.38 (Ph*C*HO); 65.42 (fullerene sp^3-C); 63.90 (fullerene sp^3-C); 48.79 (methano bridge); 37.94 (CH_2); 37.73 (CH_2); 18.91 (CH_2); 18.79 (CH_2); 13.81 (CH_3); 13.75 (CH_3); a peak at 29.69 was assigned as impurity. MALDI-TOF-MS (DHB): 1278.0 (100, M^-), 925.5 (8), 912.8 (5, C_{76}^-).

Bis[(S)-1-phenylbutyl] ([^{1}A]- or [^{1}C]-1,6-Methano[76]fullerene-77,77-dicarboxylate (**3**). Product of HPLC *Fraction Ib*: R_f (CH_2Cl_2/hexane 1:1): 0.48. UV/VIS (CH_2Cl_2): 707 (1600), 574 (1700), 433 (10100), 398 (10200), 376 (sh, 10700), 342 (sh, 16600), 272 (sh, 51800). CD (CH_2Cl_2): 777 ($\Delta\varepsilon$ = 24), 765 (20), 757 (22), 666 (−13), 619 (sh, −7), 592 (sh, 28), 574 (33), 557 (24), 543 (27), 517 (sh, 13), 485 (−40), 471 (−35), 468 (−35), 426 (−9), 397 (−67), 378 (sh, −46), 355 (−16), 328 (−97), 281 (225). ^{1}H-NMR (500 MHz, $CDCl_3$): 7.50–7.20 (*m*, 10 H); 6.07 (*t*, *J* = 7.0, 2 H); 2.20–2.10 (*m*, 2 H); 2.02–1.90 (*m*, 2 H); 1.65–1.30 (*m*, 4 H); 1.02 (*t*, *J* = 7.4, 6 H). MALDI-TOF-MS (DHB): 1279.5 (25, M^-), 1104.0 (4), 971.7 (10), 953.2 (18), 925.7 (100), 912.5 (30, C_{76}^-).

Product of HPLC *Fraction II*: R_f (CH_2Cl_2/hexane 1:1): 0.48. UV/VIS (CH_2Cl_2): 687 (4500), 573 (3600), 526 (sh, 5800), 464 (sh, 13200), 402 (23700), 329 (sh, 32200), 315 (sh, 46900), 281 (sh, 75400). CD (CH_2Cl_2): 794 ($\Delta\varepsilon$ = 37), 745 (22), 724 (11), 694 (−7), 636 (23), 572 (−79), 544 (−46), 533 (−47), 447 (81), 420 (32), 400 (114), 383 (sh, 98), 368 (sh, 84), 342 (32), 330 (50), 284 (−304). IR (KBr): 2951*m*, 2921*m*, 2863*m*, 1741*s*, 1511*w*, 1493*w*, 1453*w*, 1442*m*, 1394*w*, 1374*w*, 1256*m*, 1238*s*, 1223*s*, 1174*w*, 1100*w*, 1072*m*, 1052*w*, 1023*w*, 929*w*, 804*m*, 789*m*, 756*m*, 733*w*, 696*s*, 665*w*, 644*m*, 628*m*, 569*m*, 545*w*, 490*w*, 444*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.45–7.17 (*m*, 10 H); 6.01 (*t*, *J* = 7.1, 1 H); 6.00 (*t*, *J* = 7.1, 1 H); 2.16–2.03 (*m*, 2 H); 1.97–1.84 (*m*, 2 H); 1.53–1.43 (*m*, 2 H); 1.43–1.31 (*m*, 2 H); 0.99 (*t*, *J* = 7.4, 3 H); 0.97 (*t*, *J* = 7.4, 3 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 162.06 (C=O); 161.98 (C=O); 152.64; 151.27; 149.88; 149.36; 149.03; 148.93; 148.51; 148.23; 148.17; 148.06; 147.99; 147.92; 147.91; 147.88; 147.82; 147.79; 147.74; 147.43; 147.28; 147.21; 146.41; 145.87; 145.55; 144.86; 144.56; 144.50; 144.29; 144.11; 144.07; 144.02; 143.25; 143.09; 142.91; 142.89; 142.86; 142.48; 142.47; 142.35; 142.20; 142.09; 142.07; 141.89; 141.51; 141.33; 141.24; 140.93; 140.12; 140.05; 139.79; 139.55; 139.26; 139.02; 138.96; 138.92; 137.63; 137.41; 137.22; 136.90; 136.48; 135.67; 135.52; 135.00; 134.84; 133.83; 133.64; 133.22; 133.13; 132.32; 131.56; 130.46; 130.13; 129.66; 128.62 (arom. CH); 128.56 (arom. CH); 128.52 (arom. CH); 128.47 (arom. CH); 127.18 (2 ×) (arom. CH); 79.81 (Ph*C*HO); 79.73 (Ph*C*HO); 73.00 (fullerene sp^3-C); 71.40 (fullerene sp^3-C); 49.73 (methano bridge); 37.91 (CH_2); 37.80 (CH_2); 18.93 (CH_2); 18.91 (CH_2); 13.83 (Me); 13.81 (Me). MALDI-TOF-MS (DHB): 1279.0 (100, M^-).

Product of HPLC *Fraction III*: R_f (CH_2Cl_2/hexane 1:1): 0.48. UV/VIS (CH_2Cl_2): 678 (3100), 555 (2600), 457 (sh, 11800), 402 (18000), 345 (sh, 31400), 319 (sh, 40500), 291 (sh, 59000). CD (CH_2Cl_2): 788 ($\Delta\varepsilon$ = 13), 710 (−4), 652 (2), 561 (−84), 480 (67), 464 (75), 428 (14), 368 (154), 315 (sh, −114), 293 (−193), 279 (−135), 267 (−154). IR (KBr): 2952*m*, 2922*m*, 2852*m*, 1737*s*, 1510*w*, 1494*w*, 1452*m*, 1439*m*, 1394*w*, 1377*w*, 1260*m*, 1228*s*, 1201*m*, 1166*w*, 1135*w*, 1100*w*, 1075*m*, 1052*w*, 1031*w*, 929*w*, 804*m*, 789*w*, 756*m*, 741*w*, 720*w*, 695*s*, 670*w*, 642*m*, 570*m*, 554*m*, 490*w*, 444*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.35–7.16 (*m*, 10 H); 5.99 (*t*, *J* = 7.0, 1 H); 5.83 (*t*, *J* = 7.0, 1 H); 2.09–1.96 (*m*, 1 H); 1.94–1.80 (*m*, 2 H); 1.76–1.62 (*m*, 1 H); 1.47–1.35 (*m*, 1 H); 1.35–1.21 (*m*, 2 H); 1.20–1.09 (*m*, 1 H); 0.94 (*t*, *J* = 7.4, 3 H); 0.84 (*t*, *J* = 7.4, 3 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 162.60 (C=O); 162.55 (C=O); 152.18; 150.42; 149.16; 148.72; 148.49; 148.20; 148.00; 147.88; 147.67; 147.56; 147.28; 147.17; 147.06; 146.72; 146.48; 146.34; 146.28; 146.21; 146.12; 145.71; 145.44; 145.21; 145.12; 145.10; 144.77; 144.64; 144.54; 144.49; 144.38; 144.05 (2 ×); 143.79; 143.47; 143.33; 143.20; 143.18; 143.14; 143.02; 142.75; 142.70; 142.58; 142.54; 142.51; 142.27; 142.20; 142.01; 141.98; 141.96; 141.68; 141.43; 141.29; 141.05; 140.89; 140.38; 138.98; 138.75; 138.59; 137.87; 137.40; 137.28; 136.99; 135.62; 135.57; 135.40; 135.28; 135.04; 133.65; 133.49; 133.34; 133.01; 130.34; 130.02; 129.94; 129.91; 128.59 (arom. CH); 128.46 (arom. CH); 128.44 (arom. CH); 128.40 (arom. CH); 127.05 (2 ×) (arom. CH); 79.84 (Ph*C*HO); 79.51 (Ph*C*HO); 65.56 (fullerene sp^3-C); 64.18 (fullerene sp^3-C); 48.64 (methano bridge); 37.78 (CH_2); 37.45 (CH_2); 18.77 (CH_2); 18.64 (CH_2); 13.78 (2 ×) (Me); a peak at 29.69 was assigned as impurity. MALDI-TOF-MS (DHB): 1279.0 (84, M^-), 1277.8 (100), 925.4 (14), 912.8 (10, C_{76}^-).

Product of HPLC *Fraction IVa*: R_f (CH_2Cl_2/hexane 1:1): 0.48. UV/VIS (CH_2Cl_2): 665 (1000), 558 (1900), 437 (sh, 7900), 400 (9100), 278 (sh, 38900). CD (CH_2Cl_2): 785 ($\Delta\varepsilon$ = 9), 732 (−3), 725 (−2), 711 (−4), 707 (−4), 646 (−15), 565 (34), 542 (29), 527 (32), 445 (−31), 417 (−13), 397 (−52), 391 (−50), 380 (−53), 345 (4), 329 (−11), 283 (98). ^{1}H-NMR (500 MHz, $CDCl_3$): 7.50–7.25 (*m*, 10 H); 6.08 (*t*, *J* = 7.0, 1 H); 6.04 (*t*, *J* = 7.0, 1 H); 2.35–2.25 (*m*, 2 H); 2.15–1.95 (*m*, 2 H); 1.70–1.30 (*m*, 4 H); 1.02 (*t*, *J* = 7.4, 3 H); 0.98 (*t*, *J* = 7.4, 3 H). MALDI-TOF-MS (DHB): 1278.9 (100, M^-), 1103.8 (7), 971.7 (7), 952.8 (12), 924.8 (51), 911.3 (34, C_{76}^-).

*Bis[(*S*)-1-phenylbutyl] (*f*A)- or (*f*C)-1,6-Methano[76]fullerene-77,77-dicarboxylate* (**3**). Product of HPLC *Fraction IVb*: R_f (CH_2Cl_2/hexane 1:1): 0.48. UV/VIS (CH_2Cl_2): 710 (2100), 574 (2200), 432 (12100), 398 (12000), 376 (sh, 12500), 342 (sh, 19300), 272 (sh, 61100). CD (CH_2Cl_2): 793 ($\Delta\varepsilon$ = −13), 777 (−8), 769 (−9), 659 (30), 619 (sh, 21), 589 (−22), 574 (−27), 557 (−16), 541 (−21), 517 (sh, −8), 486 (49), 467 (sh, 41), 425 (11), 397 (74), 378 (sh, 49), 356 (16), 328 (116), 281 (−258). ^{1}H-NMR (500 MHz, $CDCl_3$): 7.41–7.25 (*m*, 10 H); 6.05 (*t*, *J* = 7.0, 2 H); 2.20–2.10 (*m*, 2 H); 2.00–1.90 (*m*, 2 H); 1.65–1.30 (*m*, 4 H); 1.00 (*t*, *J* = 7.4, 6 H). MALDI-TOF-MS (DHB): 1279.7 (90, M^-), 1104.0 (11), 971.7 (19), 952.8 (25), 925.5 (100), 912.1 (47, C_{76}^-).

Product of HPLC *Fraction V*: R_f (CH_2Cl_2/hexane 1:1): 0.48. UV/VIS (CH_2Cl_2): 689 (3300), 571 (2400), 526 (sh, 4400), 464 (sh, 11200), 402 (20700), 329 (sh, 33400), 315 (sh, 41200), 281 (sh, 67200). CD (CH_2Cl_2): 794 ($\Delta\varepsilon$ = −14), 761 (−12), 751 (−13), 724 (0), 697 (13), 638 (−9), 572 (75), 544 (44), 533 (44), 447 (−65), 420 (−25), 400 (−94), 383 (sh, −79), 368 (sh, −68), 341 (−26), 330 (−39), 284 (251). IR (KBr): 2953*m*, 2922*s*, 2853*m*, 1737*s*, 1509*w*, 1494*w*, 1455*w*, 1441*m*, 1395*w*, 1375*w*, 1256*m*, 1238*s*, 1223*s*, 1173*w*, 1099*w*, 1071*m*, 1052*w*, 1021*w*, 927*w*, 804*m*, 789*m*, 756*m*, 731*w*, 695*s*, 668*w*, 644*m*, 625*m*, 570*m*, 545*w*, 491*w*, 444*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 7.39–7.24 (*m*, 10 H); 6.01 (2*t*, *J* = 7.0, 2 H); 2.14–2.03 (*m*, 2 H); 1.95–1.82 (*m*, 2 H); 1.55–1.22 (*m*, 4 H); 0.99 (*t*, *J* = 7.4, 3 H); 0.92 (*t*, *J* = 7.4, 3 H). ^{13}C-NMR (125.8 MHz, $CDCl_3$): 162.37 (C=O); 162.30 (C=O); 152.76; 151.29; 150.01; 149.50; 149.06; 149.00; 148.72; 148.24; 148.08 (2 ×); 148.01; 147.93; 147.91 (2 ×); 147.84 (2 ×); 147.32; 146.45; 145.88;

145.55; 144.91; 144.88; 144.59; 144.52; 144.33; 144.13; 144.11; 144.09; 143.90; 143.59; 143.27; 143.19; 142.96; 142.92; 142.91; 142.87; 142.51; 142.49; 142.37; 142.22; 142.08; 142.03; 141.92; 141.52; 141.42; 141.25; 140.96; 140.47; 140.25; 139.75; 139.61; 139.47; 138.96; 138.88; 138.86; 137.72; 137.65; 137.25; 137.03; 136.56; 135.68; 135.52; 134.98; 134.86; 133.86; 133.69; 133.25; 133.09; 132.22; 131.56; 130.49; 130.19; 129.67; 128.60 (arom. CH); 128.56 (arom. CH); 128.50 (2 ×) (arom. CH); 127.14 (arom. CH); 127.10 (arom. CH); 79.85 (Ph*C*HO); 79.81 (Ph*C*HO); 73.09 (fullerene sp^3-C); 71.47 (fullerene sp^3-C); 49.46 (methano bridge); 37.70 (CH_2); 37.63 (CH_2); 18.81 (CH_2); 18.75 (CH_2); 13.81 (Me); 13.76 (Me); several peaks in the aliphatic region were assigned as impurities. MALDI-TOF-MS (DHB): 1278.8 (100, M^-), 925.6 (25), 911.4 (13, C_{76}^-).

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