Regiochemistry of Twofold Additions to [6,6] Bonds in C_{60}: Influence of the Addend-Independent Cage Distortion in 1,2-Monoadducts

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Dedicated to Professor Michael Hanack on the occasion of his 65th birthday

Abstract: Three series of regioisomeric bisadducts of C_{60}, namely, $C_{62}(anisyl)_4$ and the mixed systems $C_{62}(anisyl)_2(COOEt)_2$ and $C_{61}(COOEt)_2(NCOOEt)$, were synthesized starting from the 1,2-monoadducts $C_{61}(COOEt)_2$ (**1**), $C_{61}(anisyl)_2$ (**2**), and $C_{60}(NCOOEt)$ (**4**) by using the Bingel and Bamford–Stevens reactions, and nitrene additions. In the case of $C_{61}(COOEt)_2(NCOOEt)$ the complete series of nine possible regioisomers were isolated for the first time. For steric reasons the *cis-1* isomers of $C_{62}(anisyl)_4$ and $C_{62}(anisyl)_2(COOEt)_2$ were not formed. The transannular [6,6] bonds in the *cis-1* isomer **42** of $C_{61}(COOEt)_2(NCOOEt)$ are closed. The properties and regioselectivities of formation of these bisadducts and their monoadduct precursors were compared with those of the series $C_{62}(COOEt)_4$ and $C_{60}(NCOOEt)_2$, which we synthesized previously. In the additions to **1**, **2**, and **4** the preferred positions of attack are *e* and *trans-3* for sterically demanding addends (e.g., combinations of $C(anisyl)_2$ and $C(COOEt)_2$) and *cis-1*, *e*, and *trans-3* for sterically less demanding addends (e.g., combinations of N(COOEt) and $C(COOEt)_2$). A detailed analysis of the MO structures, the experimental and calculated geometries of monoadduct precursors, and the stabilities of reaction products leads to the conclusion that the addend-independent cage distortion itself is responsible for the observed regioselectivities of bisadduct formations.

Keywords
additions · fullerenes · regioselectivity · semiempirical calculations

Introduction

Systematic investigations into the regioselectivity of multiple 1,2-additions[1–11] to fullerenes are not only important because they reveal intrinsic chemical properties[12–14] of these carbon cages, but also because they provide the basis for designing highly symmetrical and stereochemically defined oligoadducts.[15–20] The multitude of possible aesthetically pleasing and unique architectures in which the fullerene core serves as the structure-determining tecton is unprecedented in organic chemistry. For reversible additions to the fullerene framework, the thermodynamically most stable isomer can be obtained as the only reaction product, as was shown, for example, with the synthesis of an octahedrally coordinated hexaplatinum complex of T_h symmetry.[21] For irreversible kinetically controlled addition reactions, however, mixtures of regioisomeric products are obtained. Cycloadditions to [6,6] double bonds of the fullerene framework, which are the most versatile and straightforward reactions in fullerene chemistry, fall into the latter category. For a second attack at a [6,6] bond of a C_{60} monoadduct nine different sites are available (Fig. 1). Hence, for two different addends nine regioisomeric bisadducts are in principle possible, whereas for identical addends only eight regioisomers can be considered,

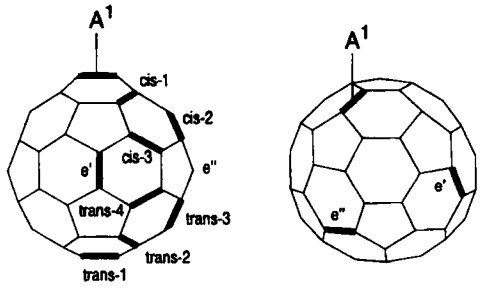

Fig. 1. Positional relationships of [6,6] double bonds relative to the first addend A^1 in a 1,2-monoadduct of C_{60}.

since attack at the *e'* and *e"* positions leads to the same product. The experimental results available at present indicate that a second irreversible attack at a [6,6] bond proceeds with a regioselective preference for *e* and *trans-3* positions for sterically demanding addends and for *e*, *trans-3*, and *cis-1* positions for sterically less demanding addends.[12] We have shown earlier that the coefficients of frontier orbitals are enhanced in these three positions (*e*, *trans-3*, *cis-1*).[4] For further additions, the regioselectivity, especially that of *e* additions, becomes successively more pronounced; this enables, for example, the synthesis of T_h-symmetric hexakisadducts in remarkably high yields.[4, 15–19] However, fundamental questions still remain open: 1) Are the observed regioselectivities of general validity or are they addend dependent? 2) Is there a difference in reac-

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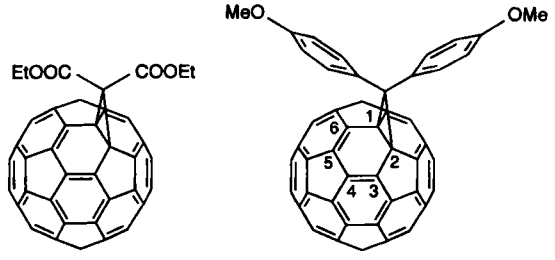
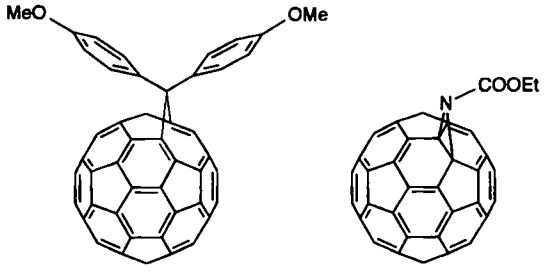
tivity between the two *e* positions? 3) What is the influence of the distortion of the fullerene cage caused by the first addend? 4) Does the distortion depend on the nature of the first addend? In order to answer these questions, we now present a comprehensive experimental and theoretical study on twofold additions to [6,6] bonds of C_{60}. Reactions of this type are the simplest and most instructive models for investigating regioselectivity and provide a basis for analyzing more complicated cases, like polyadduct formations. In order to determine the intrinsic influence of the fullerene core on the regioselectivity, special constraints like tether remote control of the first addend, which can be used to synthesize a given regioisomer in high yields,[15] were avoided as much as possible. These new comparative investigations lead to the significant result that the *distorted fullerene core itself* determines the regioselectivity of subsequent attack at the 1,2-monoadduct.

Results and Discussion

Nucleophilic cyclopropanations (Bingel reaction),[22] Bamford–Stevens reactions with dimethoxybenzophenone tosylhydrazone, and nitrene additions[8] were chosen for the synthesis of adducts with two identical or two different addends (Scheme 1). Identical reaction conditions were used to synthesize the starting materials **1**, **2**, and **4**. In the Bamford–Stevens reaction to give **2**, the [5,6] open isomer **3** was isolated in traces. Presumably, in addition to or instead of carbene additions, [3+2] cycloadditions of intermediate diazomethanes followed by N_2 extrusion are involved in the formation of **2** and **3**.[12] Quantitative rearrangement from **2** to **3** was observed in refluxing toluene.



1 **2**



3 **4**

So far, we have reported on two series of bisadducts, namely, seven regioisomers of $C_{62}(COOEt)_4$—**5**, **10**, **15**, **20**, **25**, **32**, and **37**[3]—and all eight possible regioisomers of $C_{60}(NCOOEt)_2$—**6**, **11**, **16**, **21**, **26**, **33**, **38**, and **43** (Fig. 2, Scheme 1).[8] The *cis-1* adduct of $C_{62}(COOEt)_4$ was not formed owing to the steric requirement of the addends. As another example for a series of bisadducts with two identical and symmetrical addends, we have now synthesized and isolated seven regioisomers of $C_{62}(anisyl)_4$—**7**, **12**, **17**, **22**, **27**, **34**, and **39** (Fig. 2, Scheme 1).

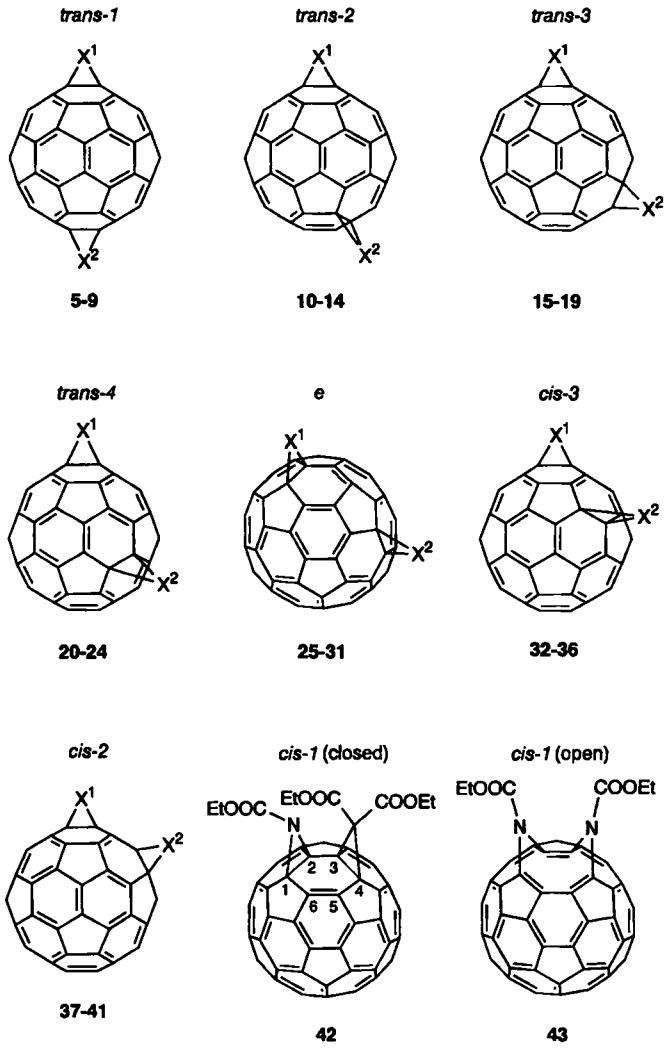


Fig. 2. Regioisomers **5**–**43** of the synthesized bisadducts $C_{62}(COOEt)_4$ [3], $C_{60}(NCOOEt)_2$ [8], $C_{62}(anisyl)_4$, $C_{62}(anisyl)_2(COOEt)_2$, and $C_{61}(COOEt)(NCOOEt)_2$. **5**, **10**, **15**, **20**, **25**, **32**, **37**: $X^1 = X^2 = C(COOEt)_2$; **6**, **11**, **16**, **21**, **26**, **33**, **38**: $X^1 = X^2 = NCOOEt$; **7**, **12**, **17**, **22**, **27**, **34**, **39**: $X^1 = X^2 = C(anisyl)_2$; **8**, **13**, **18**, **23**, **28**, **35**, **40**: $X^1 = C(anisyl)_2$, $X^2 = C(COOEt)_2$; **9**, **14**, **19**, **24**, **30**, **36**, **41**: $X^1 = NCOOEt$, $X^2 = C(COOEt)_2$; **29**: $X^1 = C(COOEt)_2$; $X^2 = C(anisyl)_2$; **31**: $X^1 = C(COOEt)_2$; $X^2 = NCOOEt$.

Also in this case the *cis-1* isomer was not formed. These bisadducts with two identical addends could also be prepared directly from C_{60}, instead of via **1**, **2**, or **4**, without changing the relative yields of the different regioisomers.

In order to distinguish between the reactivity of *e'* and *e''* positions, we isolated two series of mixed adducts, namely, eight isomers of $C_{62}(anisyl)_2(COOEt)_2$—**8**, **13**, **18**, **23**, **28**, **29**, **35**, and **40**—and nine isomers of $C_{61}(COOEt)_2(NCOOEt)$—**9**, **14**, **19**, **24**, **30**, **31**, **36**, **41**, and **42** (Fig. 2). The former series of eight regioisomers were synthesized from **1** through a Bamford–Stevens reaction or from **2** through a Bingel reaction (Scheme 1). For the preparation of $C_{61}(COOEt)_2(NCOOEt)$ a Bingel reaction with $C_{60}(NCOOEt)$ was the method of choice, since a thermal reaction of **1** with N_3COOEt also led to mixed adducts with [5,6] imino bridges,[23] which caused severe separation problems. With $C_{61}(COOEt)_2(NCOOEt)$ the complete series of nine possible [6,6] bisadducts were isolated for the first time. All bisadducts **5**–**43** shown in Figure 2 were separated by preparative HPLC on silica gel as stationary phase and either toluene or mixtures of toluene and hexane or ethyl acetate as eluent.

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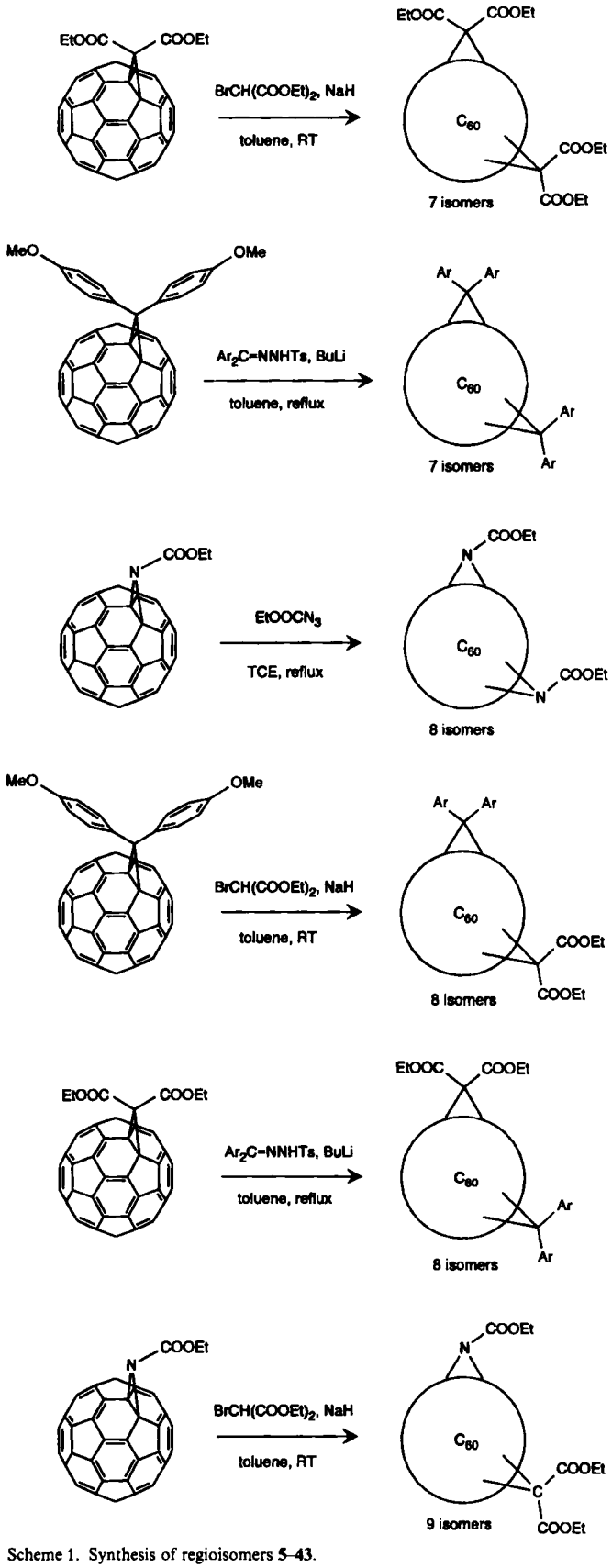

Scheme 1. Synthesis of regioisomers **5**–**43**.

The comparison of the spectroscopic data and the yields of the regioisomers of these five series of bisadducts clearly shows that the properties of isomers with the same positional relationships of the addends are closely related and that they are formed in similar relative yields (except *cis-1* adducts). This facilitates the structural assignment of the bisadducts **5**–**43** (Fig. 2), which is based on 1) the ^{1}H and ^{13}C NMR spectra from which symmetry (D_{2h}, C_{2v}, C_s, C_s, or C_1) can be deduced, 2) the comparison of their polarity[3] based on the order of elution, and 3) the comparison of the UV/Vis spectra with those of the series $C_{62}(COOEt)_4$[3] and $C_{60}(NCOOEt)_2$.[8] Based on symmetry considerations, NMR spectroscopy alone is sufficient for the unambiguous structural assignment of the *trans-1* and *e* isomers of $C_{62}(anisyl)_4$ (**7**, **27**) and the *trans-1*, *e'*, and *e''* isomers **8**, **9**, and **28**–**31** of the mixed adducts $C_{62}(anisyl)_2(COOEt)_2$ and $C_{61}(COOEt)_2(NCOOEt)$.

In the $C_{62}(anisyl)_4$ series **7** is the only isomer with D_{2h} symmetry and **27** is the only C_s-symmetrical isomer, with the methano bridges located in the mirror plane. Hence, the ^{1}H NMR spectrum of **7** contains only two doublets for the two different aromatic protons of the anisyl rings at $\delta = 8.13$ and 6.99 and one singlet for the methyl protons at $\delta = 3.85$. As expected, in the ^{13}C NMR spectrum of **7** eight signals appear between $\delta = 138$–146 and one signal at $\delta = 77.62$ for the sp^2 C atoms of the fullerene. Since the two methano bridges of **27** are located in the mirror plane, six doublets between $\delta = 6.80$ and 7.72 arise for its six magnetically different aromatic protons and three singlets at $\delta = 3.76$, 3.80, and 3.88 with an intensity ratio of 2:1:1 for the three types of methyl protons. For the same reason, **27** is the only regioisomer in the $C_{62}(anisyl)_4$ series in which the two C atoms of the methylene bridge appear as two signals at $\delta = 58.91$ and 55.77 and where the sp^3 C atoms of the fullerene core give rise to three signals at $\delta = 80.16$, 79.74, and 78.77. In all other regioisomers **12**, **17**, **22**, **34**, and **39** of $C_{62}(anisyl)_4$, which are either C_2- or C_s-symmetric, two pairs of doublets and two singlets appear for the two types of aromatic and methyl protons, and the ^{13}C NMR spectra exhibit two signals at $\delta = 78$ for the sp^3 C atoms of the fullerene core and one signal in the neighborhood of $\delta = 55$ for the C atoms of the methylene bridges. The C_2-symmetrical isomers **12**, **17**, and **34** give rise to 28 signals between $\delta = 135$ and 150, whereas for the C_s-symmetrical isomers **22** and **39** 30 signals appear in this range with two of them of half intensity. Some of the signals in the sp^2 region are closely overlapping.

The presence of two different addends in $C_{62}(anisyl)_2(COOEt)_2$ and $C_{61}(COOEt)_2(NCOOEt)$, instead of identical addends like in $C_{62}(COOEt)_4$,[3] $C_{60}(NCOOEt)_2$,[8] and $C_{62}(anisyl)_4$, leads to a lowering of symmetry for the *trans-1* isomers from D_{2h} to C_{2v} and for the other *trans* and *cis* isomers from C_2 or C_s to C_1. The C_s-symmetrical *e'* and *e''* isomers are distinguishable in the mixed adducts for the same reason. Hence, in the ^{1}H NMR spectra of the *trans-1* adducts **8** and **9** one group of signals appears for each of the two different addends: for **8** two doublets (H_{Ar}) and one singlet (CH_3) correspond to the two identical anisyl and one quartet and one triplet to the ethyl groups; for **9** two quartets and two triplets correspond to the two types of ethyl groups, since the two substituents of the methylene bridges are magnetically identical. For C_s-symmetrical **28** (*e'* isomer for **2** as precursor and *e''* isomer for **1** as precursor) two different sets of anisyl signals and one set of ethyl signals can be distinguished in the ^{1}H NMR spectrum (Fig. 3a), whereas the opposite is true of C_s-symmetrical **29** (*e''* isomer for **2** as precursor and *e'* isomer for **1** as precursor), where one set of anisyl signals and two sets of ethyl signals appear in the spectrum (Fig. 3b). In complete analogy, ^{1}H NMR spectroscopy can be used to distinguish between the two equatorial isomers **30** and **31** of $C_{61}(COOEt)_2(NCOOEt)$, since the spectrum of **30** (*e'* isomer with respect to aziridine) shows two different ethyl groups and the spectrum of **31** (e'' isomer) three different ethyl groups.

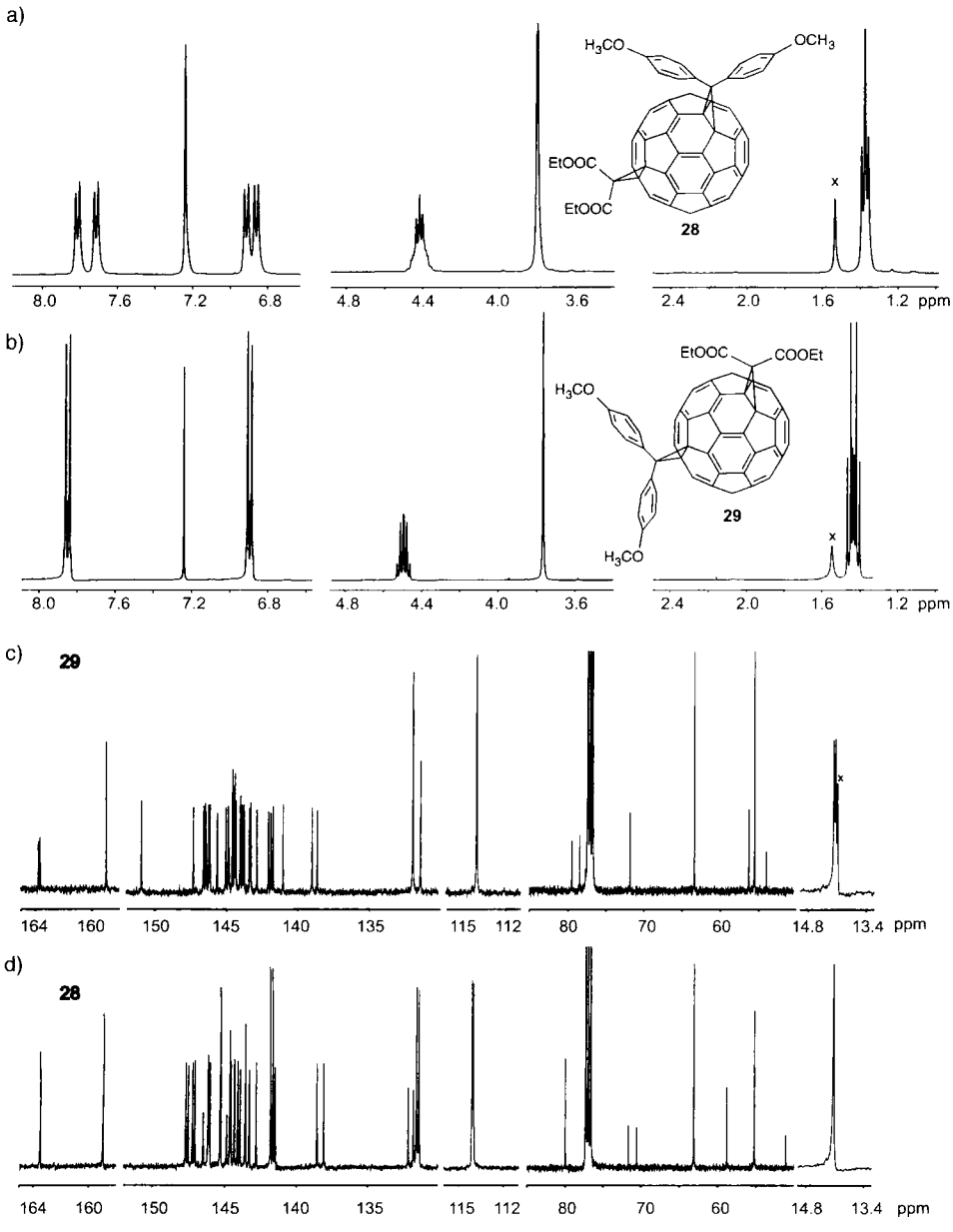

Fig. 3. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of a) **28** and b) **29** and ^{13}C NMR spectra (100 MHz, $CDCl_3$) of c) **29** and d) **28** (× denotes an impurity).

The different *e* isomers **28–31** can be distinguished analogously by ^{13}C NMR spectroscopy. In the following we illustrate this with the examples of **28** and **29**. In the ^{13}C NMR spectrum of **29** the signals of the two different ethoxycarbonyl groups are split, whereas the C atoms of the two anisyl groups are magnetically identical (Fig. 3d). The opposite is observed in the spectrum of **28** (Fig. 3c), that is, splitting of the signal for the anisyl C atoms and only one set of signals for the identical ethoxy carbonyl groups. Likewise, the sp^3 C atoms of the fullerene core located within the mirror plane give rise to two signals, which appear at $\delta = 78$ (dianisylmethylene bridgeheads) for **29** and at $\delta = 71$ (diethoxycarbonylmethylene bridgeheads) for **28**. The sp^3 C atoms of the [6,6] bond perpendicular to the mirror plane appear as one signal at $\delta = 72$ (diethoxycarbonylmethylene bridgeheads) for **29** and at $\delta = 80$ (dianisylmethylene bridgeheads) for **28**. Analogous results are obtained from the analysis of the ^{13}C NMR spectra of **30** and **31**. The NMR spectra of the other regioisomers in the two series $C_{62}(anisyl)_2(COOEt)_2$ and $C_{61}(COOEt)_2(NCOOEt)$ reflect their C_1 symmetry, like four (**13**, **18**, **23**, **35**, **40**) or three (**14**, **19**, **24**, **36**, **41**, **42**) groups of signals for the four or three magnetically inequivalent groups in the side chains, four signals for each of the bridgehead C atoms of the fullerene core in the sp^3 region, and up to 56 sometimes closely overlapping signals for the sp^2 fullerene C atoms. Of special interest is the ^{13}C NMR spectrum of the *cis*-1 isomer **42** of $C_{61}(COOEt)_2(NCOOEt)$. Whereas the signals of the sp^3 fullerene C atoms carrying the imino bridge appear around $\delta = 80$ in the other regioisomers of $C_{61}(COOEt)_2$-(NCOOEt) as well as in the monoadduct $C_{60}NCOOEt$ (**4**) and in the bisadducts $C_{60}(NCOOEt)_2$,[8] those of **42** are dramatically shifted upfield and appear at $\delta = 68.02$ and 58.30. Also, the signal of C-4 in **42** appears shifted upfield by 6 ppm. This behavior is in line with that of other closed *cis-1* adducts[6, 8] and may be due to a release of strain energy in this region of the fullerene sphere. The *cis-1* connectivity in **42** was unambiguously proven by using 100% ^{15}N-labeled material. In the ^{13}C NMR spectrum of [^{15}N]**42** the signals of C atoms carrying the imino bridge at $\delta = 68.02$ and 58.30 are split into two doublets with $^1J(C,N) = 4.5$ and 5.5 Hz, and the neighboring sp^3 C atom (C-3) appears also as a doublet at $\delta = 73.40$ with $^2J(C,N) = 2$ Hz. This ^2J coupling is only consistent with a *cis-1* addition pattern of **42**. The ^1J coupling constant for the ^{15}N atom and the carbonyl C atom in the side chain in [^{15}N]**42** is 13 Hz. The chemical shifts of the bridgehead C atoms of **42** clearly show that the corresponding bridged [6,6] bonds are closed, whereas those of **43**[8] are open. This is the expected result and, indeed, according to AM1 calculations, the closed form of **42** is more stable than the open form by 2 kcal mol^{-1}.

As we pointed out earlier,[3, 8] the electronic properties of a given bisadduct depend mostly on the addition pattern rather than on the nature of the addend; for example, the UV/Vis spectra of analogous regioisomers in the series $C_{62}(COOEt)_4$[3] and $C_{60}(NCOOEt)_2$[8] are almost identical. Especially, the characteristic features in region between 400 and 800 nm can be used as a fingerprint for the identification of a given regioisomer. Hence, it is also possible to use UV/Vis spectroscopy for a further structural assignment of the remaining newly synthesized bisadducts in each series, such as the *trans-2*, *trans-3*, and *trans-4* as well as the *cis-2* and *cis-3* isomers. The UV/Vis spectra of $C_{62}(anisyl)_2(COOEt)_2$ and $C_{61}(COOEt)_2(NCOOEt)$ are shown in Figure 4.

The order of elution in the HPLC (silica gel) of the $C_{62}(anisyl)_4$ series is the same as those of the $C_{62}(COOEt)_4$[3]

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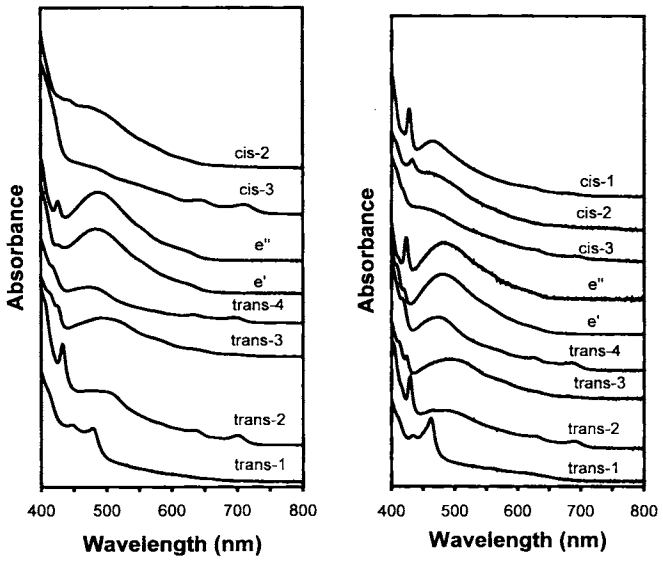

Fig. 4. Electronic absorption spectra (CH_2Cl_2) of the isolated regioisomers of $C_{62}(anisyl)_4$ (left) and $C_{61}(COOEt)_2(NCOOEt)$ (right).

and $C_{60}(NCOOEt)_2$,[8] which is expected based on the increasing polarity with decreasing distance of the addends. However, the order of elution in the cases of the mixed adducts of $C_{62}(anisyl)_2(COOEt)_2$ and $C_{61}(COOEt)_2(NCOOEt)$ is less predictable. Although, most of the regioisomers in these series elute in the expected order, there are two exceptions: 1) *cis-1* $C_{61}(COOEt)_2(NCOOEt)$ (**42**) elutes between *cis-2*- and *cis-3*-$C_{61}(COOEt)_2$-(NCOOEt) (**36** and **41**), possibly a concentration effect since the abundance of **42** is higher than those of **36** and **41** by an order of magnitude and 2) the *e* isomer **28** elutes between the corresponding *trans-2* and *trans-3* derivatives **13** and **18**, whereas the other *e* isomer **29** elutes as expected after the *trans-4* compound **23**. In conclusion, based on the experimental data an unambiguos structural assignment is possible for the *trans-1*, *e*, and *cis-1* isomers of $C_{62}(anisyl)_4$, $C_{62}(anisyl)_2(COOEt)_2$, and $C_{61}(COOEt)_2(NCOOEt)$, and an adequately reliable assignment is given for the corresponding isomers of these newly synthesized compounds.

For a comparative analysis of the regioselectivities of these twofold additions to C_{60} (Scheme 1) the relative yields of the various bisadducts **5**–**43** are represented in Figure 5. These typical product distributions show the following characteristics:

1) The product distributions are not statistical (one possibility for a *trans-1* attack, two possibilities for *e'* or *e''* attacks, and four possibilities each for attack at the other *trans* or *cis* positions).
2) In most cases the preferred reaction products are *e* isomers followed by the *trans-3* isomers.
3) The *cis-1* isomers are formed only if the steric requirement of the addends allows their suitable arrangement in close proximity (e.g., at least one of the addends must be an imino bridge, which, unlike the methano bridge, contains only one flexible side chain).
4) If their formation is possible, the *cis-1* adducts together with the *e* isomers are obtained as the major products.
5) Attack at the *e''* position is preferred over attack at the *e'* position.
6) The regioselectivity of bisadduct formation is less pronounced when more extreme reaction conditions are used (e.g., less regioselectivity for nitrene additions in refluxing 1,1,2,2-tetrachloroethane[8] than reactions with diethyl bromomalonate at room temperature[3]).

For an interpretation of these experimental findings it is useful to distinguish between the properties of the reaction products **5**–**43** (bisadducts), such as their relative stabilities, and the geometric and electronic structure of the starting materials **1**, **2**, and **4**. The AM1-calculated stabilities of various bisadducts are listed in Table 1. In order to reduce CPU time and to avoid problems related to multiple local minima, ethyl esters were replaced by methyl esters and anisyl by phenyl substituents in

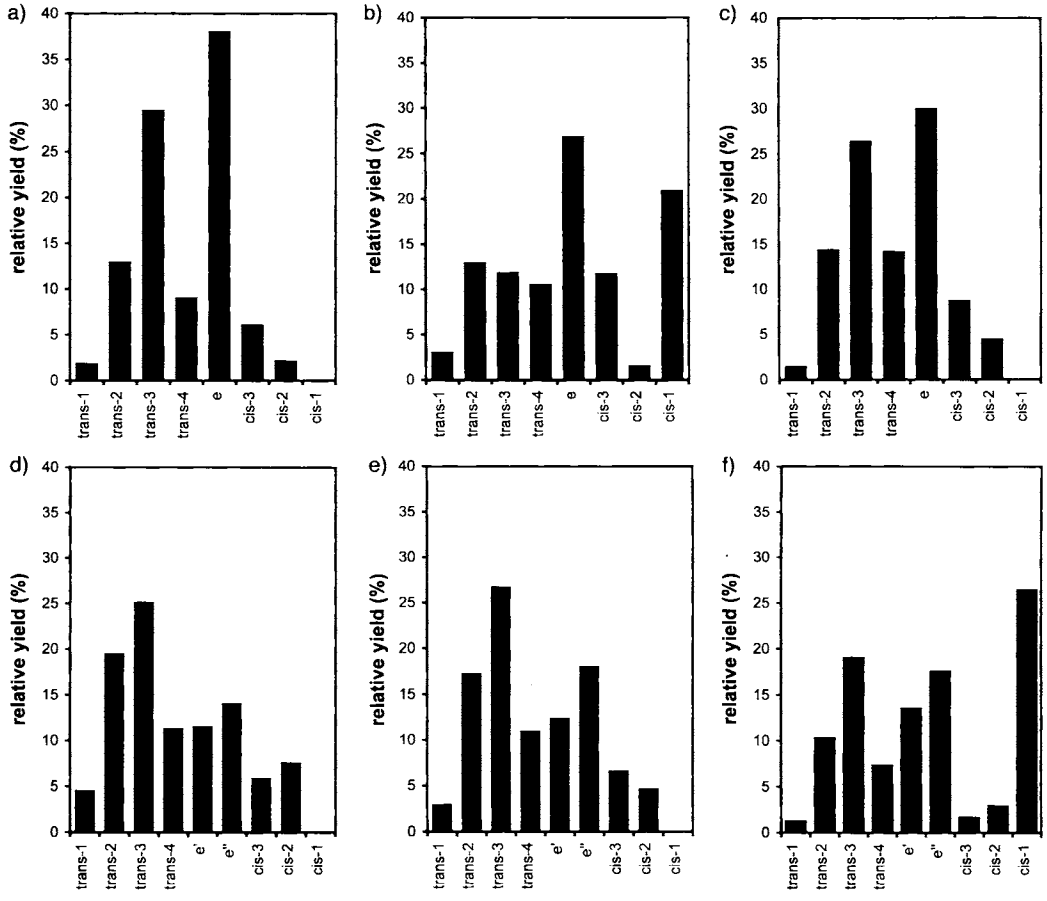

Fig. 5. Relative yields of the isolated regioisomeric bisadducts of a) $C_{62}(COOEt)_4$ [3], b) $C_{60}(NCOOEt)_2$ [8], c) $C_{62}(anisyl)_4$, d) $C_{62}(anisyl)_2(COOEt)_2$ with **1** as precursor, e) $C_{62}(anisyl)_2(COOEt)_2$ with **2** as precursor, and f) $C_{61}(COOEt)_2$-(NCOOEt).

Table 1. Relative stabilities (AM 1_{HOF}) in kcal mol^{-1} of the possible regioisomers of bisadducts with two identical and two different addends.

	$C_{62}(COOMe)_4$ [3]	$C_{62}(phenyl)_4$	$C_{60}(NCOOMe)_2$ [8]	$C_{61}(COOMe)_2$-(NCOOMe)
trans-1	0.2	0.2	4.4	1.3
trans-2	0.2	0.3	4.5	1.2
trans-3	0.1	0.2	4.3	1.1
trans-4	0.0	0.1	4.4	1.1
e'	0.0 [a]	0.0 [a]	4.2 [a]	0.8 [b]
e''	0.0 [a]	0.0 [a]	4.2 [a]	0.8 [c]
cis-3	1.3	2.3	5.9	3.7
cis-2	1.8	3.3	6.7	3.8
cis-1	17.7	24.9	0.0	0.0

[a] *e'* and *e''* isomers are identical. [b] *e'* isomer relative to $C_{61}(COOEt)_2$ as precursor molecule. [c] *e''* isomer relative to $C_{61}(COOEt)_2$ as precursor molecule.

the model compounds for the bisadduct series $C_{62}(COOEt)_4$,[3] $C_{60}(NCOOEt)_2$,[8] $C_{62}(anisyl)_4$, and $C_{61}(COOEt)_2(NCOOEt)$.

Two important results emerge from these calculations: 1) in bisadducts with two dialkoxycarbonylmethylene or diarylmethylene groups the *cis-1* adducts are considerably less stable than the other isomers, which exhibit very similar AM 1 heats of formation; 2) in bisadducts with at least one imino addend the *cis-1* isomers are not destabilized compared to the other isomers (the *cis-1* and, to a lesser extent, the *e* isomers are slightly more stable and the *cis-2* and *cis-3* isomers slightly less stable than the average). In all cases the *trans* isomers have about the same calculated heat of formation. As can be seen from the space-filling model (Fig. 6, left), the instability of a *cis-1* isomer like *cis-1*-$C_{62}(anisyl)_4$ is simply due to the steric interactions between the addends, which are forced into close proximity and lead to considerable deformations of typical bond angles. When at least one imino addend is present (Fig. 6, right), a strain-free arrangement can be attained avoiding unfavorable interactions between the addends in a low-energy invertomer.

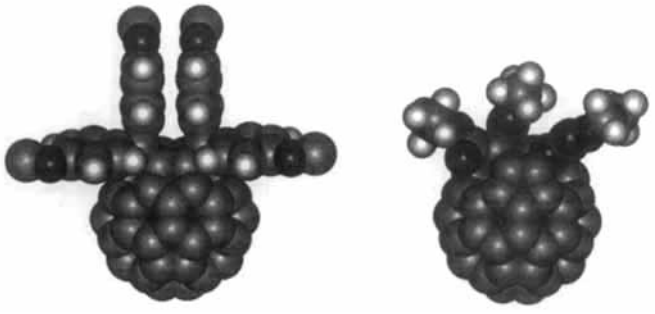

Fig. 6. Space-filling models of the AM 1-calculated structures (HyperChem 4.5) of hypothetical *cis-1*-$C_{62}(anisyl)_4$ (left) and *cis-1*-$C_{61}(COOEt)_2(NCOOEt)$ (**42**) (right).

Analogous behavior was observed for the various regioisomers of $C_{60}H_4$,[5] where, apart from eclipsing H interactions, no additional strain due to the addends is present. The corresponding *cis-1* adduct is the major product formed by a twofold hydroboration followed by hydrolysis. AM 1 calculations[24] predict *cis-1*-$C_{60}H_4$ to be of about the same stability as the other *cis* and *trans* isomers and the *e* isomer to be somewhat more stable. According to ab initio calculations (HF/3-21G)[5] the *cis*-1 is the most stable, followed by the *e* isomer.

In order to evaluate the influence of the geometric and electronic properties of the starting materials on the observed product distributions, we analyzed a variety of experimental and calculated monoadduct structures and carried out frontier-orbital investigations. We were able to grow single crystals of $C_{61}(anisyl)_2$ (**2**) from toluene/CS_2 solutions suitable for X-ray analysis (Fig. 7). The compound crystallizes without inclusion of solvents in the monoclinic space group $P2(1)/m$. In the crystal, **2** has C_s symmetry. The molecules of **2** are arranged in sheets with exact antiparallel arrangement of the addends (Fig. 7, bottom). The closest intermolecular distance between the C atoms

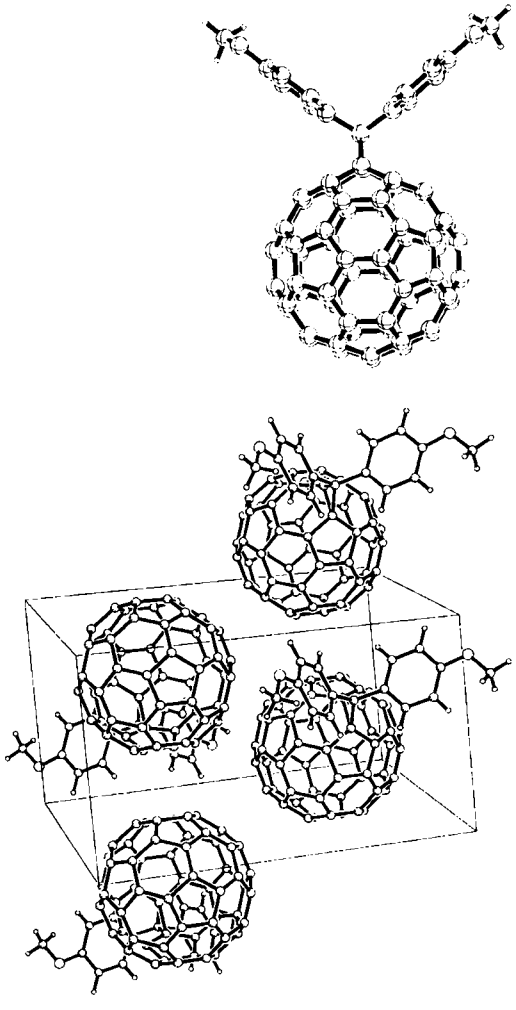

Fig. 7. X-ray crystal structure of **2** (top) and crystal packing in the unit cell (bottom).

of two carbon cages with the same sheet is 3.35 Å and between two molecules of two neighboring sheets 4.48 Å. The average value of the [5,6] bonds is 1.451 Å and that of the [6,6] bonds, excluding the cyclopropanated [6,6] bond between C-1 and C-2, 1.388 Å; this clearly shows that the [5]radialene-type structure of the fullerene cage is preserved. Bond lengths of the corresponding [6,6] bonds in **2** are listed in Table 2.

The bond length between C-1 and C-2 in **2** is comparatively long (1.625 Å). However, the most significant result is that the *e''* bonds (1.362 Å) and the *cis-1* bonds (1.377 Å) are the shortest, while the *e'* bonds (1.396 Å) and the other [6,6] bonds (1.388–1.401 Å) are considerably longer. As a consequence, the diameters of the carbon cage perpendicular and parallel to the cyclopropane ring differ by 0.17 Å, and the sphere is flattened along the axis $a_\perp$ perpendicular to the cyclopropanated double bond (Fig. 8). The comparison of the X-ray structure of **2** with those of $C_{61}(COOEt)_2$ (**1**)[25], the methanofullerene **44**,[26] and the Diels–Alder adduct **45**[27] (Table 2) shows that this particu-

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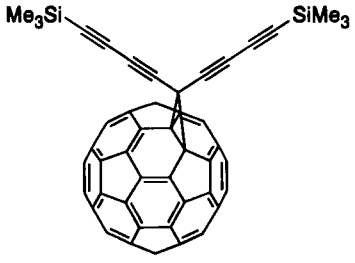
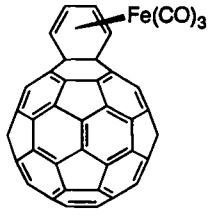
Table 2. Comparison of [6,6] bond lengths (in Å, mean values) of the monoadducts $C_{61}(anisyl)_2$ (**2**), $C_{61}(COOEt)_2$ (**1**) [25], **44** [26], and **45** [27] determined by X-ray crystallography.

	2	1	44	45
trans-1	1.401	1.384	1.385	1.381
trans-2	1.388 [a]	1.391 [a]	1.392 [a]	1.389 [a]
trans-3	1.399 [a]	1.395 [a]	1.393 [a]	1.399 [a]
trans-4	1.388 [a]	1.386 [a]	1.391 [a]	1.391 [a]
e'	1.396 [b]	1.394 [b]	1.394 [b]	1.385 [b]
e''	1.362 [b]	1.384 [b]	1.379 [b]	1.379 [b]
cis-3	1.394 [a]	1.389 [a]	1.391 [a]	1.398 [a]
cis-2	1.390 [a]	1.406 [a]	1.393 [a]	1.390 [a]
cis-1	1.377 [a]	1.379 [a]	1.378 [a]	1.367 [a]
C(1)–C(2)	1.625	1.606	1.574	1.586

[a] Mean value of four bond lengths. [b] Mean value of two bond lengths.



44



45

lar distortion of the fullerene cage, caused by the binding of the first addend, is a general phenomenon and that it is not restricted to monoadduct **2**. In each case the fullerene cage is distorted in the same way, namely, by a significant shortening of the *cis-1* bonds and, to a somewhat lesser extent, of the *e''* bonds, leading to a compression of the sphere along the $a_\perp$ axis.

Qualitatively, the same trend is predicted by calculations (AM1). In Figure 9 the deviations of [6,6] bond lengths from that of C_{60} are represented for a variety of adducts including **1** and **4**. A typical shortening of the *cis-1* and, to a lesser extent, of the *e''* bonds can be seen, which is almost independent of the nature of the addend. Another trend to emerge from the analysis of these data is that the *cis-2* and *cis-3* bonds are somewhat elongated and that the opposing hemisphere is less disturbed. Similarly to the geometrical distortions, the polarization (AM1 Mulliken charges) of the carbon framework in these monoadducts is somewhat larger in the neighborhood of the first addend, but essentially zero in the opposing hemisphere.

We pointed out earlier[4] that coefficients of frontier orbitals in $C_{61}(COOEt)_2$ (**1**) at a given [6,6] bond can be correlated with the preference for attack at this site. The LUMO coefficients in a precursor molecule are expected to influence the product distribution of nucleophilic additions (e.g., Bingel reaction) and of 1,3-dipolar cycloadditions (e.g., addition of diazo compounds), and the HOMO coefficients those of, for example, nitrene or carbene additions and also of 1,3-dipolar cycloadditions. These are the possible mechanisms for the reactions in Scheme 1. MO calculations (AM1; SPARTAN 4.0) on $C_{61}(anisyl)_2$ (**2**) (Fig. 10) and $C_{60}NCOOEt$ (**4**), which are the precursor molecules used in this study, reveal that they exhibit essentially the same MO structure as **1**, except that the HOMO of **2** is addend-centered. Hence, in order to discuss the effects related to the fullerene cage in **1**, **2**, and **4** the HOMO − 1 of **2** has to be compared with the HOMO of **1** and **4**, etc. To facilitate discussion the HOMOs of **1** and **4** and the HOMO − 1 of **2** are denoted as $HOMO_{cage}$. The MO structures of **1**, **2**, and **4** exhibit the following characteristics: In the $HOMO_{cage}$ the highest coefficients are located at the *e''* bonds, followed by the *cis-1* bonds. In the $HOMO_{cage}$ − 1 the highest coefficients are located in *e'*, *trans-3*, and *cis-2* positions. The highest LUMO coefficients are found in *e'* and the next lower in *trans-3* and *cis-2* positions, and enhanced HOMO + 1 coefficients again are located in *e''* positions, followed by *cis-1* and *trans-2*. Only in the LUMO + 2 do the *trans-1*, *trans-4*, and *cis-3* bonds also exhibit enhanced coefficients. For **2** the energy differences between $HOMO_{cage}$/$HOMO_{cage}$ − 1, LUMO/HOMO + 1, and HOMO + 1/HOMO + 2 are 0.17, 0.09, and 0.12 eV, respectively. Essentially the same values were obtained for **1**[4] and **4**. Although, the shortest *e''* and *cis-1* bonds exhibit enhanced coefficients in the frontier orbitals, a direct correlation between bond lengths and orbital coefficients can be ruled out, since, for example, [6,6] bonds of unchanged length, like *trans-3*, can also have high coefficients. However, the addend-independent regularities in both the geometrical and the MO properties of

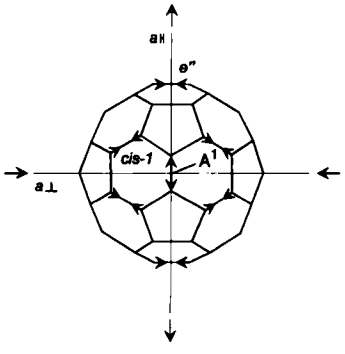


Fig. 8. Schematic representation of the cage distortion in a 1,2-monoadduct of C_{60}.

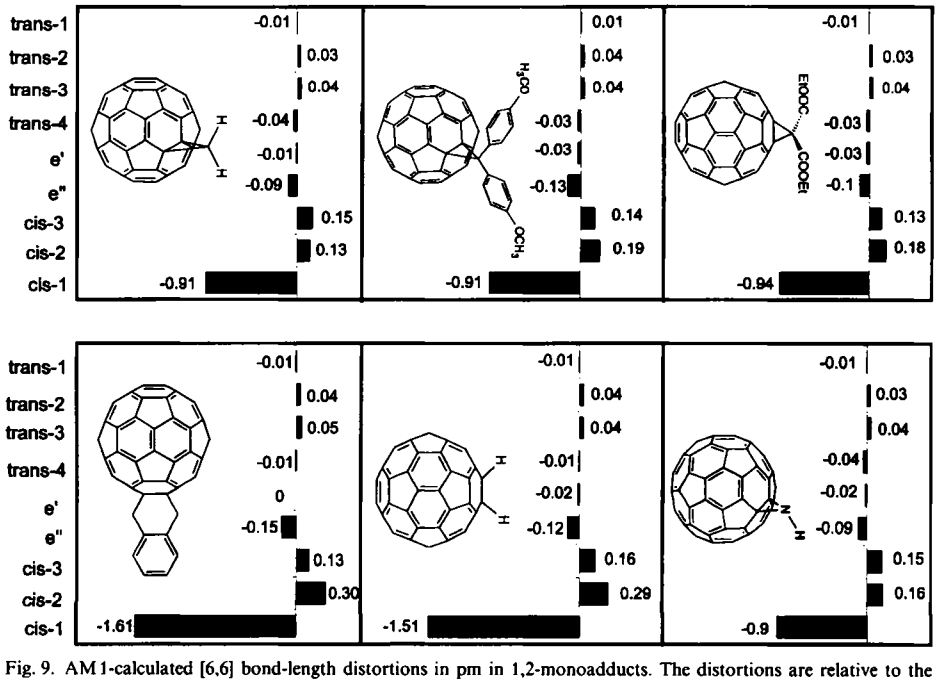


Fig. 9. AM1-calculated [6,6] bond-length distortions in pm in 1,2-monoadducts. The distortions are relative to the calculated length of the [6,6] bonds of free C_{60}.

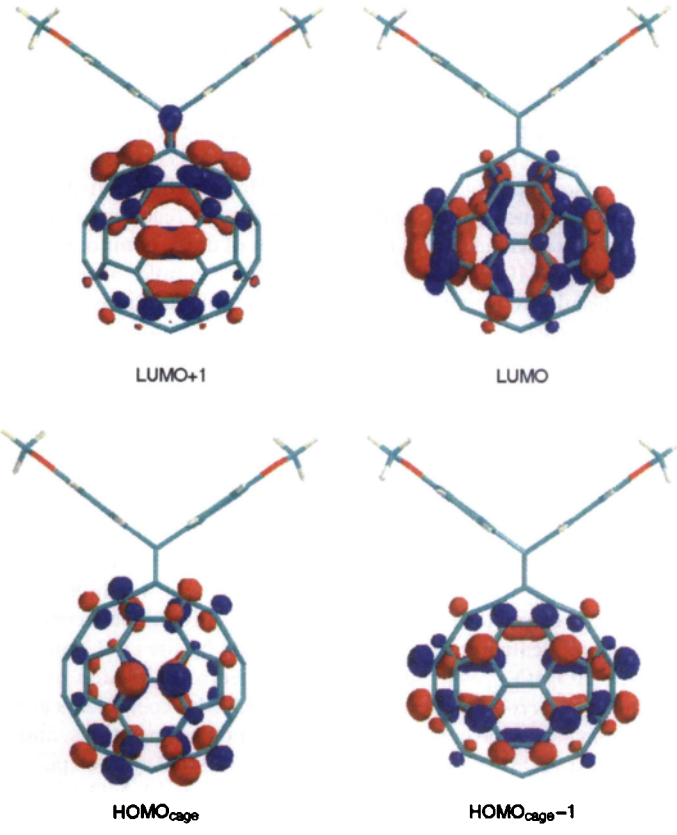


Fig. 10. AM1-calculated frontier orbitals of **2**: HOMO$_{cage}$−1, HOMO$_{cage}$, LUMO, and LUMO+1.

[6,6] monoadducts of C_{60} strongly imply that the typical cage distortions are in general responsible for the characteristic MO structures.

Summary and Conclusion

In this study three series of regioisomeric bisadducts of C_{60}, namely, $C_{62}(anisyl)_4$ and the mixed systems $C_{62}(anisyl)_2(COOEt)_2$ and $C_{61}(COOEt)_2(NCOOEt)$, were synthesized by using Bingel and Bamford–Stevens reactions as well as nitrene additions (Scheme 1). In the case of $C_{61}(COOEt)_2(NCOOEt)$ the complete series of nine possible regioisomers were isolated for the first time. For steric reasons the *cis-1* isomers of $C_{62}(anisyl)_4$ and $C_{62}(anisyl)_2(COOEt)_2$ were not formed. As expected, the transannular [6,6] bonds in the *cis-1* isomer **42** of $C_{61}(COOEt)_2(NCOOEt)$ are closed; this result nicely complements our investigations on opening and closure of [6,6] bonds in *cis-1* adducts of C_{60}.[8] The results concerning the properties and the yields of the newly synthesized bisadducts as well as their monoadduct precursors were compared with those of the series $C_{62}(COOEt)_4$[3] and $C_{60}(NCOOEt)_2$,[8] which we synthesized previously.

The addition reactions to [6,6] double bonds of 1,2-monoadducts of C_{60} do not proceed statistically, but with a preference for attack at the *e* and *trans-3* bonds for sterically demanding addends (e.g., combinations of $C(anisyl)_2$ and $C(COOEt)_2$) and at *e*, *trans-3*, and *cis-1* bonds for sterically less demanding addends (e.g., combinations of N(COOEt) and $C(COOEt)_2$) (Fig. 5). Attack at the *e''* position is slightly preferred over that at *e'* (Fig. 5). This leads to the prediction that T_h-symmetrical hexaadducts of C_{60} can only be synthesized in reasonable yields by direct attack when the addends are sterically demanding. Otherwise, attack at the *cis-1* position competes with the desired successive *e* additions. For the three types of addition reactions investigated in this study, the product distributions are always very similar, regardless of which monoadduct was used as starting material. This demonstrates that the characteristic regioselectivities are essentially independent of the nature of the first addend. The first addend only has significant influence when it is bulky, so that it can prevent the *cis-1* adducts from forming, which are otherwise the preferred reaction products. Semiempirical (Table 1) and ab initio calculations predict *cis-1* isomers (for sterically nondemanding addends) and *e* isomers (for all addends) to be the most stable. However, thermodynamic arguments alone are not sufficient to explain the regioselectivities, since these calculated differences in stabilities are small. In particular, there are almost no differences between the various *trans* isomers, although, for example, the formation of *trans-3* adducts is significantly preferred over the formation of *trans-4* adducts (Fig. 5). Valuable information can be deduced from the experimental (Table 2, Fig. 7) and calculated (Fig. 9) geometries of 1,2-monoadducts, since the first addend leads to a characteristic cage distortion, which is independent of the nature of the addend. The *cis-1* bonds and, to a lesser extent, the *e''* bonds are shorter than the average. One reason for the characteristic shortening of the *cis-1* bonds could be the removal of electron delocalization within the six-membered ring under consideration. Consequently, the fullerene cage is compressed along the $a_\perp$ axis. It is to be expected that shorter double bonds within the fullerene cage are located within areas with enhanced local strain. Hence, these bonds should be the most reactive and, moreover, additions to these bonds should cause the most efficient release of strain energy leading to the thermodynamically most stable regioisomers. Relief of strain is an important driving force in fullerene chemistry.[12] Indeed, neglecting possible steric interactions between the addends, the *cis-1* and *e* isomers are thermodynamically most stable. On the other hand, the enhanced HOMO coefficients (Fig. 10) confirm the prediction that these bonds, which are most compressed, should be the most kinetically reactive. However, these geometry considerations do not account for the fact that attack at other double bonds, such as *e'* and *trans-3* bonds, which are not shortened compared to the [6,6] bonds in C_{60}, are also regioselectively preferred. Significantly, the latter bonds exhibit enhanced frontier orbital coefficients. Hence, there is no general correlation between the length and the reactivity of a given bond. However, pronounced reactivities of [6,6] double bonds in monoadducts can satisfactorily be correlated with a combination of enhanced frontier orbital coefficients, more reactive compressed [6,6] double bonds, and the possibility of forming thermodynamically more stable addition products. These three aspects can be related to one and the same phenomenon, namely, the characteristic cage distortion present in 1,2-monoadducts of C_{60}. In other words, it is the addend-independent cage distortion itself that is responsible for the observed regioselectivity of twofold additions to [6,6] double bonds in [60]fullerene.

Experimental Section

^1H and ^{13}C NMR: Bruker AC250, JEOL JNM EX400, and JEOL JNM GX400; MS: Varian MAT 311A (EI) and Finnigan TSQ70 (FAB); IR: Bruker IFS48; UV/Vis: Shimadzu UV3102 PC; HPLC preparative: Shimadzu SIL10A, SPD10A, CBM10A, LC8A, FRC10A (Grom-Sil 100Si, NP1, 5 μ, 25 × 4.6); TLC (Riedel-de Haën, silica gel 60 F_{254}). Reagents were prepared according to common procedures. Materials and solvents were obtained from commercial suppliers and were used without further purification. All reactions were carried out under a positive pressure of nitrogen. Products were isolated where possible by flash column chromatography (silica gel 60, particle size 0.04–0.063 nm, Merck).

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Crystal data of 2: $M_r = 946.86$; monoclinic; space group $P2_1/n$; cell dimensions: $a = 9.823(1)$, $b = 17.513(2)$, $c = 11.229(1)$ Å; $\beta = 101.81(1)°$; $V = 1902.3(3)$ Å^3; $\rho_{calcd} = 1.653$ Mg m^{-3}; $Z = 2$; $F(000) = 960$; graphite monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å); $T = 193(2)$ K. Data were collected with a Enraf–Nonius MACH 3 diffractometer equipped with a rotating anode on a crystal with the dimensions $0.1 \times 0.3 \times 0.3$ mm. Data collecting range: $4.0 < 2\theta < 50.0°$. Of a total of 3275 collected reflections, 3083 were unique and 1859 with $I > 2\sigma(I)$ observed. The structure was solved by direct methods using SHELXS86. 356 parameters were refined with all data by full-matrix least-squares on F^2 using SHELXL93 (G. M. Sheldrick, Göttingen 1993). All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were fixed in idealized positions by using a riding model. Final R values: $R1 = 0.0678$ [$(I > 2\sigma(I)$] and $wR2 = 0.1613$ (all data) with $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR2 = \sum w|(F_o^2 - F_c^2)^2|/\sum w(F_o^2)^2)^{0.5}$; largest peak (0.255 e Å^{-3}) and hole (-0.261 e Å^{-3}). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1220-33. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: Int. code +(1223)336-033; e-mail: teched@chemcrys.cam.ac.uk).

1,2-Di(*p*-methoxyphenyl)methano-1,2-dihydro[60]fullerene (2): *n*-Butyllithium (135 mg, 2.089 mmol) was added to a solution of 4,4'-dimethoxybenzophenone tosylhydrazone (810 mg, 1.973 mmol) in toluene (150 mL) to deprotonate the tosyl hydrazone. [60]Fullerene (1 g, 1.4 mmol) in toluene (500 mL) was then added, and the mixture was heated up to 110 °C for 1 h. The product was separated from unreacted C_{60} and from the [5,6] adduct (**3**) and higher adducts by flash chromatography with a mixture of toluene/hexane 4/1 as eluent. For the complete separation of **2** from **3** preparative HPLC with a mixture of toluene and hexane in a ratio of 3:2 as eluent was used (yield: 35% **2**).

2: ^{1}H NMR (250 MHz, CS_2 +10% $CDCl_3$, 25 °C): $\delta = 3.82$ (s, 6H, CH_3), 6.92 (d, J(H,H) = 8.54 Hz, 4H, Ph), 7.90 (d, J(H,H) = 8.54, 4H, Ph); ^{13}C NMR (62.9 MHz, CS_2 +10% $CDCl_3$, 25 °C): $\delta = 54.58$ (2C, CH_3), 56.75 (1C, methylene-C), 78.99, 113.77 (4C, Ph-C), 113.77 (2C, Ph-C), 131.46 (4C, Ph-C), 137.90, 140.47, 141.72, 141.80, 142.54, 142.60, 143.44, 143.92, 144.17, 144.29, 144.71, 144.76, 144.93, 147.89, 158.76 (2C, Ph-C); IR (KBr): $\tilde{\nu} = 3004$, 2953, 2928, 2904, 1607, 1510, 1250, 824, 550, 525 cm^{-1}; UV/Vis (CH_2Cl_2): $\lambda_{max} = 327$, 431 nm; MS (EI): $m/z = 946$ [M^+].

3: ^{1}H NMR (250 MHz, CS_2 +10% $CDCl_3$, 25 °C): $\delta = 3.71$ (s, 3H, CH_3), 3.80 (s, 3H, CH_3), 6.67 (d, J(H,H) = 8.85 Hz, 2H, Ph), 6.95 (d, J(H,H) = 8.85 Hz, 2H, Ph), 7.21 (d, J(H,H) = 8.85 Hz, 2H, Ph), 7.90 (d, J(H,H) = 8.85 Hz, 2H, Ph); ^{13}C NMR (62.9 MHz, CS_2 +10% $CDCl_3$, 25 °C): $\delta = 54.49$ (1C, CH_3), 54.65 (1C, CH_3), 63.52 (1C, methylene-C), 113.32 (2C, Ph-C), 114.22 (2C, Ph-C), 127.40 (2C, Ph-C), 130.39 (2C, Ph-C), 134.11 (2C, Ph-C), 135.48 (2C, Ph-C), 137.20, 137.68, 138.03, 138.56, 139.81, 140.19, 140.28, 140.44, 140.96, 141.76, 142.31, 142.65, 142.74, 142.77, 142.81, 143.23, 143.26, 143.35, 143.43, 143.45, 143.60, 143.92, 144.14, 144.37, 144.80, 147.02, 157.94 (1C, Ph-C), 158.10 (1C, Ph-C); IR (KBr): $\tilde{\nu} = 3446$, 3030, 2995, 2950, 2924, 2900, 1604, 1581, 1509, 1458, 14436, 1250, 816, 536, 527 cm^{-1}; UV/Vis (cyclohexane): $\lambda_{max} = 263$, 330, 528 nm; MS (EI): $m/z = 946$ [M^+], 720 (C_{60}).

Bis[di(*p*-methoxyphenyl)methano]tetrahydro[60]fullerenes (7, 12, 17, 22, 27, 34, and 39): Same procedure as described for the synthesis of **2**. The separation from C_{60}, monoadducts **2** and **3**, and higher adducts was carried out by flash chromatography with a mixture of toluene/hexane 4/1 as eluent. For a complete rearrangement to [6,6] adducts, the mixture of bisadducts was heated in toluene under reflux for 6 h. The separation of isomers was achieved by preparative HPLC with a mixture of toluene and hexane in a ratio of 7:3 as eluent. The relative yields (HPLC) of the bisadducts are: 1.5% **7** (*trans-1*), 14.46% **12** (*trans-2*), 26.44% **17** (*trans-3*), 14.24% **22** (*trans-4*), 30.03% **27** (*ε*), 8.81% **34** (*cis-3*), 4.51% **39** (*cis-2*).

7 (*trans-1*): ^{1}H NMR (250 MHz, CS_2 +10% $CDCl_3$, 25 °C): $\delta = 3.85$ (s, 12H, CH_3), 6.99 (d, J(H,H) = 8.85 Hz, 8H, Ph), 8.13 (d, J(H,H) = 8.85, 8H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 49.86$ (2C, methylene-C), 55.35 (4C, CH_3), 77.62, 114.25 (8C, Ph-C), 132.02 (8C, Ph-C), 132.33 (4C, Ph-C), 138.29, 141.20, 143.46, 143.83, 144.37, 145.18, 145.54, 146.04, 159.06 (4C, Ph-C); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 238 (61000), 270 (48800), 330 (16700), 412 (3100), 455 (1800), 489 (1700) nm; MS (FAB/3-NBA): $m/z = 1172$ [M^+], 720 (C_{60}).

12 (*trans-2*): ^{1}H NMR (250 MHz, CS_2 +10% $CDCl_3$, 25 °C): $\delta = 3.79$ (s, 6H, CH_3), 3.89 (s, 6H, CH_3), 6.87 (d, J(H,H) = 8.85 Hz, 4H, Ph), 7.04 (d, J(H,H) = 8.55 Hz, 4H, Ph), 7.89(d, J(H,H) = 8.55 Hz, 4H, Ph), 8.11 (d, J(H,H) = 8.54 Hz, 4H, Ph); ^{13}C NMR (62.9 MHz, CS_2 +10% $CDCl_3$, 25 °C): $\delta = 54.04$ (2C, CH_3), 54.87 (2C, CH_3), 54.97 (2C, methylene-C), 78.08, 78.34, 113.83 (4C, Ph-C), 114.06 (4C, Ph-C), 131.56 (4C, Ph-C), 131.88 (4C, Ph-C), 136.46 (2C, Ph-C), 136.61 (2C, Ph-C), 139.56, 139.79, 141.10, 141.60, 141.77, 141.94, 142.07, 142.35, 143.06, 143.35, 143.51, 143.92, 144.03, 144.17, 144.54, 144.96, 145.02, 145.12, 145.17, 145.42, 145.55, 145.76, 146.46, 146.93, 151.04, 158.73 (2C, Ph-C), 158.95 (2C, Ph-C); IR (KBr): $\tilde{\nu} = 3030$, 2996, 2950, 2832, 1607, 1581, 1510, 1460, 1439, 1249, 820, 546, 525 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 238 (72000), 265 (65000), 325 (20000), 388 (5000), 435 (2521), 503 (1319), 640 (322), 707 (175) nm; MS (FAB/3-NBA): $m/z = 1172$ [M^+], 1066, 840, 720 (C_{60}).

17 (*trans-3*): ^{1}H NMR (250 MHz, CS_2 +10% $CDCl_3$, 25 °C): $\delta = 3.77$ (s, 6H, CH_3), 3.83 (s, 6H, CH_3), 6.89 (d, J(H,H) = 8.85 Hz, 4H, Ph), 6.99 (d, J(H,H) = 8.85 Hz, 4H, Ph), 7.85 (d, J(H,H) = 8.55 Hz, 4H, Ph), 7.98 (d, J(H,H) = 8.80 Hz, 4H, Ph); ^{13}C NMR (62.9 MHz, CS_2 +10% $CDCl_3$, 25 °C): $\delta = 55.21$ (2C, CH_3), 55.28 (2C, CH_3), 56.15 (2C, methylene-C), 78.95, 79.46, 113.95 (4C, Ph-C), 114.08 (4C, Ph-C), 131.67 (4C, Ph-C), 131.70 (4C, Ph-C), 131.79 (2C, Ph-C), 131.89 (2C, Ph-C), 137.57, 138.12, 140.58, 141.26, 141.50, 141.58, 141.83, 142.42, 143.13, 143.32, 143.46, 143.79, 143.99, 144.10, 144.31, 144.49, 145.26, 145.32, 146.17, 146.46, 147.45, 148.55, 148.99, 149.25, 149.65, 158.86 (2C, Ph-C), 158.99 (2C, Ph-C); IR (KBr): $\tilde{\nu} = 3426$, 3031, 2996, 2950, 2928, 2833, 1607, 1581, 1511, 1460, 1438, 1250, 820, 550, 527 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 242 (89000), 258 (79000), 378 (8000), 419 (3000), 431 (2000), 496 (1000), 586 (700), 643 (200) nm; MS (FAB/3-NBA): $m/z = 1172$ [M^+], 1066, 840, 720 (C_{60}).

22 (*trans-4*): ^{1}H NMR (250 MHz, CS_2 +10% $CDCl_3$, 25 °C): $\delta = 3.73$ (s, 6H, CH_3), 3.83 (s, 6H, CH_3), 6.79 (d, J(H,H) = 8.85 Hz, 4H, Ph), 6.91 (d, J(H,H) = 8.85 Hz, 4H, Ph), 7.76 (d, J(H,H) = 8.54 Hz, 4H, Ph), 7.85 (d, J(H,H) = 8.85 Hz, 4H, Ph); ^{13}C NMR (62.9 MHz, CS_2 +10% $CDCl_3$, 25 °C): $\delta = 54.93$ (2C, CH_3), 55.15 (2C, CH_3), 55.29 (2C, methylene-C), 78.10, 78.42, 113.95 (4C, Ph-C), 114.08 (4C, Ph-C), 131.53 (4C, Ph-C), 131.72 (4C, Ph-C), 131.95 (2C, Ph-C), 132.00 (2C, Ph-C), 134.94, 137.56, 138.01, 139.64, 140.71, 141.29, 141.80, 142.04, 142.22, 142.25, 142.60, 142.98, 143.01, 143.73, 144.79, 144.86, 144.89, 145.01, 145.08, 145.23, 145.30, 145.33, 145.39, 145.49, 145.61, 146.23, 146.84, 146.93, 147.84, 148.16, 158.83 (2C, Ph-C), 158.96 (2C, Ph-C); IR (KBr): $\tilde{\nu} = 3031$, 2996, 22950, 2928, 1607, 1581, 1510, 1461, 1249, 819, 553, 524 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 241 (68000), 268 (53000), 322 (19000), 477 (1000), 637 (300), 701 (100) nm; MS (FAB/3-NBA): $m/z = 1172$ [M^+], 1064, 840, 720 (C_{60}).

27 (*e*): ^{1}H NMR (250 MHz, CS_2 +10% $CDCl_3$, 25 °C): $\delta = 3.76$ (s, 6H, CH_3), 3.80 (s, 3H, CH_3), 3.88 (s, 3H, CH_3), 6.80 (d, 4H, Ph), 6.84 (d, 2H, Ph), 6.90 (d, 2H, Ph), 7.72 (m, 8H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 55.22$ (2C, CH_3), 55.27 (1C, CH_3), 55.40 (1C, CH_3), 55.77 (1C, methylene-C), 58.91 (1C, methylene-C), 80.16, 79.74, 78.77, 113.83 (4C, Ph-C), 113.97 (2C, Ph-C), 114.25 (2C, Ph-C), 131.42 (2C, Ph-C), 131.46 (2C, Ph-C), 131.59 (2C, Ph-C), 131.81 (2C, Ph-C), 132.28 (2C, Ph-C), 132.43 (2C, Ph-C), 137.91, 138.80, 140.92, 141.22, 141.45, 141.56, 141.93, 142.79, 143.24, 143.53, 143.92, 144.14, 144.25, 144.45, 144.51, 144.61, 144.72, 145.11, 145.31, 146.06, 146.13, 146.18, 146.33, 146.77, 147.03, 147.32, 147.54, 150.53, 158.83 (2C, Ph-C), 158.92 (1C, Ph-C), 158.98 (1C, Ph-C); IR (KBr): $\tilde{\nu} = 3032$, 2995, 2951, 2927, 2832, 1606, 1580, 1510, 1460, 1439, 1249, 819, 552, 527 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 242 (68000), 315 (22000), 363 (9000), 402 (3000), 432 (2000), 496 (1000) nm; MS (FAB/3-NBA): $m/z = 1172$ [M^+], 919, 766, 720 (C_{60}).

34 (*cis-3*): ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 3.78$ (s, 6H, CH_3), 3.79 (s, 6H, CH_3), 6.83 (d, J(H,H) = 3.06 Hz, 4H, Ph), 6.87 (d, J(H,H) = 2.75 Hz, 4H, Ph), 7.70 (d, J(H,H) = 8.54 Hz, 4H, Ph), 7.84 (d, J(H,H) = 8.54 Hz, 4H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 52.73$ (2C, CH_3), 55.22 (2C, CH_3), 55.35 (2C, methylene-C), 77.58, 79.92, 113.94 (4C, Ph-C), 114.23 (4C, Ph-C), 131.35 (4C, Ph-C), 131.46 (2C, Ph-C), 131.62 (4C, Ph-C), 131.79 (2C, Ph-C), 136.99, 137.27, 137.51, 140.26, 140.65, 140.85, 141.89, 142.46, 142.49, 142.77, 143.10, 143.50, 144.27, 144.36, 144.45, 144.54, 144.58, 144.63, 144.81, 144.89, 145.00, 145.09, 145.31, 145.36, 145.43, 146.18, 146.31, 146.73, 158.59 (2C, Ph-C), 158.77 (2C, Ph-C); IR (KBr): $\tilde{\nu} = 2923$, 2853, 1607, 1511, 1460, 1249, 820 cm^{-1}; UV/Vis (CH_2Cl_2): $\lambda_{max} = 240$ (78000), 262 (66900), 321 (24600), 658 (290), 724 (160) nm; MS (FAB/3-NBA): $m/z = 1172$ [M^+].

39 (*cis-2*): ^{1}H NMR (250 MHz, $CDCl_3$, 25 °C): $\delta = 3.76$ (s, 6H, CH_3), 3.88 (s, 6H, CH_3), 6.80 (d, J(H,H) = 8.85 Hz, 4H, Ph), 6.87 (d, J(H,H) = 8.85 Hz, 4H, Ph), 7.44 (d, J(H,H) = 8.85 Hz, 4H, Ph), 7.67 (d, J(H,H) = 8.85 Hz, 4H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 55.16$ (2C, CH_3), 55.18 (2C, CH_3), 55.25 (2C, methylene-C), 74.70, 78.08, 113.79 (4C, Ph-C), 114.07 (4C, Ph-C), 130.86 (2C, Ph-C), 131.20 (2C, Ph-C), 131.36 (4C, Ph-C), 132.02 (4C, Ph-C), 132.23, 133.53, 135.50, 135.80, 139.67, 141.21, 141.26, 142.72, 143.33, 143.62, 143.59, 143.74, 143.82, 143.87, 144.14, 144.27, 144.77, 144.89, 145.15, 145.35, 145.49, 145.79, 145.82, 146.07, 146.07, 147.37, 147.42, 149.67, 151.41, 158.83 (2C, Ph-C), 158.92 (2C, Ph-C); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 242 (77000), 266 (64000), 322 (23500), 385 (8800), 488 (2400) nm; MS (FAB/3-NBA): $m/z = 1172$ [M^+].

Di(ethoxycarbonyl)methanodi(*p*-methoxyphenyl)methanotetrahydro[60]fullerenes (8, 13, 18, 23, 28, 29, 35, and 40):

Method A: 4,4'-Dimethoxybenzophenone tosylhydrazone (196.8 mg, 0.48 mmol), deprotonated with *n*-butyllithium (37.2 mg, 0.57 mmol), in toluene (30 mL) was added to a solution of 1,2-di(ethoxycarbonyl)methano-1,2-dihydro[60]fullerene (**1**) (400 mg, 0.48 mmol) in toluene (300 mL). The reaction mixture was heated to 110 °C for 3 h, and the bisadducts were separated from by-products and starting material by flash chromatography with toluene/hexane 8/2 as eluent. The bisadducts themselves were separated by preparative HPLC with toluene as eluent for the

more polar isomers (*cis-2*, *cis-3*, *e''*) and a mixture of dichloromethane and hexane in a ratio of 3:2 for the less polar isomers (*trans-4*, *e'*, *trans-3*, *trans-2*, *trans-1*). The relative yields (HPLC) of the bisadduct isomers are: 4.60% **8** (*trans-1*), 19.53% **13** (*trans-2*), 25.16% **18** (*trans-3*), 11.39% **23** (*trans-4*), 11.58% **28** (*e'*), 14.14% **29** (*e''*), 5.95% **35** (*cis-3*), 7.65% **40** (*cis-2*).

Method B: Diethyl bromomalonate (88.45 mg, 0.38 mmol) and sodium hydride (88.8 mg, 3.8 mmol, 10 equiv) were added to a solution of **2** (350 mg, 0.37 mmol) in toluene (1 L). After being stirred for 8 h, the mixture was worked up as described above in Method A. The relative yields are: 3.01% **8** (*trans-1*), 17.28% **13** (*trans-2*), 26.8% **18** (*trans-3*), 11.0% **23** (*trans-4*), 12.45% **28** (*e'*), 18.08% **29** (*e''*), 6.66% **35** (*cis-3*), 4.72% **40** *cis-2*.

8 (*trans-1*): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.56 (t, J(H,H) = 7.14 Hz, 6H, CH_3), 3.86 (s, 6H, OCH_3), 4.61 (q, J(H,H) = 7.17 Hz, 4H, CH_2), 6.99 (d, J(H,H) = 8.84 Hz, 4H, Ph), 8.12 (d, J(H,H) = 8.77 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 14.21 (2C, CH_3), 49.84 (2C, OCH_3), 54.71 (2C, methylene-C), 62.79 (2C, CH_2), 69.65, 76.25, 113.99 (4C, Ph-C), 131.63 (4C, Ph-C), 131.76 (2C, Ph-C), 138.16, 138.95, 141.02, 142.97, 143.18, 143.33, 143.59, 144.25, 144.58, 145.03, 145.07, 145.17, 145.87, 158.93 (2C, Ph-C), 163.07 (2C, CO); IR (KBr): $\tilde{\nu}$ = 2924, 2853, 1745, 1607, 1511, 1461, 1299, 1248, 820, 560, 525 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 235 (39000), 262 (32000), 269 (32000), 324 (11000), 411 (1600), 446 (1000), 480 (1000) nm; MS(EI): m/z = 1104 [M^+].

13 (*trans-2*): ^{1}H NMR (400 MHz, C_6D_6 + 10% CS_2, 25 °C): δ = 1.46 (t, J(H,H) = 7.08 Hz, 3H, CH_3), 1.59 (t, J(H,H) = 7.16 Hz, 3H, CH_3), 3.78 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 4.46 (q, J(H,H) = 7.17 Hz, 2H, CH_2), 4.63 (q, J(H,H) = 7.25 Hz, 2H, CH_2), 6.88 (d, J(H,H) = 8.61 Hz, 2H, Ph), 7.04 (d, J(H,H) = 8.45 Hz, 2H, Ph), 7.90 (d, J(H,H) = 8.56 Hz, 2H, Ph), 8.11 (d, J(H,H) = 8.75 Hz, 2H, Ph); ^{13}C NMR (100 MHz, C_6D_6 + 10% CS_2, 25 °C): δ = 14.55 (1C, CH_3), 14.69 (1C, CH_3), 49.84 (1C, OCH_3), 54.53 (1C, OCH_3), 54.75 (1C, methylene-C), 55.19 (1C, methylene-C), 62.88 (1C, OCH_2), 63.07 (1C, OCH_2), 71.06, 71.57, 78.46, 78.84, 114.26 (2C, Ph-C), 114.47 (2C, Ph-C), 131.63 (2C, Ph-C), 131.65 (2C, Ph-C), 131.97 (1C, Ph-C), 132.36 (1C, Ph-C), 137.09, 137.18, 137.76, 137.91, 140.16, 140.28, 140.36, 140.83, 141.58, 141.70, 142.11, 142.27, 142.34, 142.42, 142.48, 142.75, 142.92, 143.17, 143.27, 143.43, 143.93, 144.06, 144.14, 144.42, 144.54, 144.67, 145.01, 145.18, 145.35, 145.48, 145.54, 145.61, 145.65, 145.85, 145.90, 146.03, 146.09, 146.22, 146.29, 146.32, 146.41, 147.19, 147.29, 148.44, 151.22, 159.29 (1C, Ph-C), 159.48 (1C, Ph-C), 162.54 (1C, CO), 162.91 (1C, CO); IR (KBr): $\tilde{\nu}$ = 2958, 2932, 2835, 1744, 1606, 1510, 1461, 1441, 1299, 1246, 821, 559, 526 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 237 (91000), 263 (90000), 321 (29000), 386 (7000), 433 (2000), 502 (1000) nm; MS(EI): m/z = 1104 [M^+].

18 (*trans-3*): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.39 (t, J(H,H) = 7.02 Hz, 3H, CH_3), 1.48 (t, J(H,H) = 7.29 Hz, 3H, CH_3), 3.75 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 4.45 (q, J(H,H) = 6.86 Hz, 2H, CH_2), 4.55 (m, 2H, CH_2), 6.88 (d, J(H,H) = 8.80 Hz, 2H, Ph), 6.99 (d, J(H,H) = 8.59 Hz, 2H, Ph), 7.85 (d, J(H,H) = 8.77 Hz, 2H, Ph), 7.98 (d, J(H,H) = 8.44 Hz, 2H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 14.06 (1C, CH_3), 14.15 (1C, CH_3), 51.34 (1C, OCH_3), 55.16 (1C, OCH_3), 55.25 (1C, methylene-C), 56.42 (1C, methylene-C), 63.16 (1C, OCH_2), 63.27 (1C, OCH_2), 71.05, 71.51, 79.16, 79.69, 114.01 (2C, Ph-C), 114.14 (2C, Ph-C), 131.63 (2C, Ph-C), 131.73 (2C, Ph-C), 131.84 (2C, Ph-C), 137.70, 138.25, 138.52, 139.14, 140.33, 140.71, 141.43, 141.51, 141.60, 141.77, 141.80, 141.99, 142.07, 142.31, 142.47, 142.56, 143.12, 143.20, 143.40, 143.44, 143.49, 143.57, 143.86, 143.99, 144.10, 144.15, 144.27, 144.34, 144.58, 144.64, 145.31, 145.35, 145.38, 145.44, 145.71, 145.94, 146.04, 146.19, 146.23, 146.28, 146.37, 146.40, 146.49, 146.59, 146.66, 146.87, 147.28, 147.51, 148.70, 149.17, 149.41, 149.73, 158.99 (1C, Ph-C), 159.12 (1C, Ph-C), 163.69 (1C, CO), 163.73 (1C, CO); IR (KBr): $\tilde{\nu}$ = 2954, 2833, 1747, 1607, 1511, 1461, 1440, 1299, 1250, 821, 560, 521 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 243 (45000), 251 (44000), 317 (13000), 377 (4000), 498 (900) nm; MS(EI): m/z = 1104 [M^+].

23 (*trans-4*): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.36 (t, J(H,H) = 7.01 Hz, 3H, CH_3), 1.45 (t, J(H,H) = 7.15 Hz, 3H, CH_3), 3.77 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 4.39 (m, 2H, CH_2), 4.51 (m, 2H, CH_2), 6.88 (d, J(H,H) = 8.83 Hz, 2H, Ph), 6.96 (d, J(H,H) = 8.71 Hz, 2H, Ph), 7.85 (d, J(H,H) = 8.74 Hz, 2H, Ph), 7.92 (d, J(H,H) = 8.97 Hz, 2H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 14.05 (1C, CH_3), 14.12 (1C, CH_3), 49.69 (1C, OCH_3), 55.02 (1C, OCH_3), 55.21 (1C, methylene-C), 55.25 (1C, methylene-C), 63.07 (1C, OCH_2), 63.17 (1C, OCH_2), 70.56, 70.96, 78.40, 78.69, 114.06 (2C, Ph-C), 144.16 (2C, Ph-C), 131.65 (2C, Ph-C), 131.74 (2C, Ph-C), 131.81 (1C, Ph-C), 131.91 (1C, Ph-C), 134.89, 135.77, 137.71, 138.08, 138.42, 139.03, 139.58, 140.78, 140.89, 141.49, 141.87, 141.91, 141.98, 142.01, 142.05, 142.16, 142.19, 142.24, 142.33, 142.68, 142.70, 142.79, 143.05, 143.12, 143.41, 143.71, 143.87, 144.17, 144.71, 144.92, 144.95, 144.99, 145.06, 145.14, 145.33, 145.37, 145.44, 145.52, 145.63, 145.74, 145.83, 145.91, 146.09, 146.11, 146.42, 147.02, 147.06, 147.22, 148.06, 148.28, 159.00 (1C, Ph-C), 159.08 (1C, Ph-C), 163.80 (1C, CO), 163.81 (1C, CO); IR (KBr): $\tilde{\nu}$ = 2978, 2931, 2903, 1746, 1607, 1510, 1461, 1441, 1298, 1248, 821, 553, 529 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 242 (89000), 272 (69000), 323 (28000), 484 (2000) nm; MS(EI): m/z = 1104 [M^+].

28 (*e'*): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.37 (t, J(H,H) = 7.04 Hz, 6H, CH_3), 3.79 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 4.41 (m, 4H, CH_2), 6.86 (d, J(H,H) = 8.95 Hz, 2H, Ph), 6.92 (d, J(H,H) = 8.63 Hz, 2H, Ph), 7.71 (d, J(H,H) = 8.87 Hz, 2H, Ph), 7.82 (d, J(H,H) = 8.32 Hz, 2H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 14.07 (2C, CH_3), 51.08 (1C, methylene-C), 55.23 (2C, OCH_3), 58.81 (1C, methylene-C), 63.13 (2C, OCH_2), 70.59, 71.68, 80.02, 114.07 (2C, Ph-C), 114.15 (2C, Ph-C), 131.42 (2C, Ph-C), 131.59 (2C, Ph-C), 131.81 (1C, Ph-C), 132.18 (1C, Ph-C), 138.143, 138.62, 141.56, 141.71, 141.87, 142.90, 143.38, 143.64, 144.02, 144.18, 144.43, 144.65, 144.71, 144.94, 145.36, 145.39, 146.09, 146.15, 146.23, 146.55, 147.12, 147.28, 147.57, 147.73 (1C, Ph-C), 159.07 (1C, Ph-C), 163.61 (2C, CO); IR (KBr): $\tilde{\nu}$ = 2952, 2903, 2831, 1746, 1607, 1511, 1460, 1439, 1300, 1251, 820, 558, 524 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 244 (83000), 311 (30607), 361 (12000), 402 (4100), 489 (2500) nm; MS(EI): m/z = 1104 [M^+].

29 (*e''*): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.42 (t, J(H,H) = 7.17 Hz, 3H, CH_3), 1.45 (t, J(H,H) = 7.17 Hz, 3H, CH_3), 3.77 (s, 6H, OCH_3), 4.49 (m, 4H, CH_2), 6.89 (d, J(H,H) = 8.80 Hz, 4H, Ph), 7.85 (d, J(H,H) = 8.82 Hz, 4H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 14.07 (1C, CH_3), 14.11 (1C, CH_3), 53.60 (1C, methylene-C), 55.21 (2C, OCH_3), 55.95 (1C, methylene-C), 63.14 (2C, OCH_2), 71.67, 78.38, 79.41, 113.97 (4C, Ph-C), 131.35 (2C, Ph-C), 131.88 (4C, Ph-C), 138.59, 138.97, 141.01, 141.72, 141.87, 142.04, 142.86, 143.29, 143.38, 143.76, 143.88, 143.99, 144.03, 144.32, 144.40, 144.42, 144.56, 144.80, 144.87, 145.03, 145.63, 146.14, 146.23, 146.40, 146.45, 146.58, 147.30, 150.98, 159.01 (2C, Ph-C), 163.74 (1C, CO), 163.85 (1C, CO); IR (KBr): $\tilde{\nu}$ = 3031, 2977, 2929, 2833, 1745, 1606, 1510, 1460, 1440, 1299, 1247, 820, 558, 523 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 254 (108000), 313 (38000), 360 (15000), 401 (4000), 427 (2500), 486 (2000) nm; MS(EI): m/z = 1104 [M^+].

35 (*cis-3*): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C and 400 MHz, CD_2Cl_2, 25 °C): δ = 1.38 (q, J(H,H) = 7.10 Hz, 6H, CH_3), 3.78 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 4.29 (m, 1H, CH_2), 4.45 (m, 3H, CH_2), 6.84 (d, J(H,H) = 8.65 Hz, 2H, Ph), 6.91 (d, J(H,H) = 8.68 Hz, 2H, Ph), 7.73 (d, J(H,H) = 8.61 Hz, 2H, Ph), 7.84 (d, J(H,H) = 8.54 Hz, 2H, Ph); ^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C): δ = 13.95 (2C, CH_3), 48.28 (1C, OCH_3), 53.04 (1C,OCH_3), 55.28 (1C, methylene-C), 55.35 (1C, methylene-C), 63.15 (1C, OCH_2), 63.23 (1C, OCH_2), 69.45, 71.98, 76.62, 80.13, 113.92 (2C, Ph-C), 114.17 (2C, Ph-C), 129.23 (1C, Ph-C), 131.99 (1C, Ph-C), 131.61 (2C, Ph-C), 131.99 (2C, Ph-C) 133.99, 136.99, 137.18, 137.52, 137.87, 138.41, 138.84, 140.53, 140.64, 140.98, 141.08, 141.13, 141.41, 142.01, 142.07, 142.20, 142.40, 142.62, 142.64, 142.67, 143.09, 143.34, 143.41, 143.66, 143.71, 144.13, 144.42, 144.48, 144.51, 144.60, 144.72, 144.84, 144.87, 144.93, 144.98, 145.03, 145.10, 145.13, 145.17, 145.19, 145.24, 145.54, 145.63, 145.67, 145.69, 146.53, 146.56, 147.26, 159.21 (1C, Ph-C), 159.30 (1C, Ph-C), 162.88 (1C, CO), 163.66 (1C, CO); IR (KBr): $\tilde{\nu}$ = 3031, 2929, 2833, 1746, 1607, 1510, 1461, 1439, 1298, 1247, 820, 558, 524 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 260 (73000), 318 (24000), 416 (2000), 490 (1000) nm; MS(EI): m/z = 1104 [M^+].

40 (*cis-2*): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C and 400 MHz, CD_2Cl_2, 25 °C): δ = 1.42 (t, J(H,H) = 7.14 Hz, 3H, CH_3), 1.44 (t, J(H,H) = 7.35 Hz, 3H, CH_3), 3.74 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 4.48 (m, 4H, CH_2), 6.84 (d, J(H,H) = 8.73 Hz, 2H, Ph), 6.91 (d, J(H,H) = 8.58 Hz, Ph), 7.72 (d, J(H,H) = 8.87 Hz, 2H, Ph), 7.86 (d, J(H,H) = 8.70 Hz, 2H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 14.07 (2C, CH_3), 49.24 (1C, OCH_3), 54.46 (1C, OCH_3), 55.17 (1C, methylene-C), 55.23 (1C, methylene-C), 63.17 (2C, OCH_2), 67.19, 70.48, 75.73, 77.70, 113.83 (2C, Ph-C), 114.00 (2C, Ph-C), 130.73 (1C, Ph-C), 131.10 (1C, Ph-C), 131.56 (2C, Ph-C), 131.97 (2C, Ph-C), 134.08, 135.86, 136.10, 136.85, 137.37, 139.14, 139.82, 140.99, 141.18, 141.31, 141.49, 142.37, 142.63, 142.83, 143.12, 143.48, 143.60, 143.65, 143.71, 143.89, 143.98, 143.99, 144.24, 144.34, 144.38, 144.64, 144.74, 144.87, 145.17, 145.25, 145.27, 145.33, 145.49, 145.76, 145.77, 145.86, 146.02, 146.17, 146.30, 147.32, 147.39, 147.48, 147.62, 148.56, 149.38, 151.81, 158.91 (1C, Ph-C), 159.06 (1C, Ph-C), 163.36 (1C, CO), 163.77 (1C, CO); IR (KBr): $\tilde{\nu}$ = 2978, 2902, 2833, 1746, 1606, 1510, 1460, 1440, 1298, 1248, 820, 557, 527 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 249 (520000), 320 (166000), 379 (59000), 444 (15000), 483 (13000) nm; MS(EI): m/z = 1104 [M^+].

Ethoxycarbonylliminodi(ethoxycarbonyl)methanotetrahydro[60]fullerenes (9, 14, 19, 24, 30, 31, 36, 41, and 42): Diethyl bromomalonate (31 mL, 0.186 mmol, 1 equiv) and sodium hydride (2.79 mmol, 15 equiv) were added at room temperature to a solution of 1,2-(ethoxycarbonylimino)-1,2-dihydro[60]fullerene (**4**) (150 mg, 0.186 mmol) in toluene (100 mL). After reaction mixture had been stirred for 3 d, excess sodium hydride was destroyed with diluted sulfuric acid. The bisadducts were purified from by-products by flash chromatography with toluene as eluent and then separated by preparative HPLC with a mixture of toluene/ethyl acetate 99.5/0.5 as eluent. The relative yields (HPLC) of the bisadducts **9**, **14**, **19**, **24**, **30**, **31**, **36**, **41**, **42** are: 1.24% **9** (*trans-1*), 10.26% **14** (*trans-2*), 19.01% **19** (*trans-3*), 7.34% **24** (*trans-4*), 13.54% **30** (*e'*), 17.55% **31** (*e''*), 1.64% **36** (*cis-3*), 2.97% **41** (*cis-2*) and 26.45% **42** (*cis-1* adduct).

9 (*trans-1*): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.68 (q, J(H,H) = 7 Hz, 2H, CH_2), 4.65 (q, J(H,H) = 7 Hz, 4H, CH_2), 1.58 (t, J(H,H) = 7 Hz, 3H, CH_3), 1.55 (t, J(H,H) = 7 Hz, 6H, CH_3); ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): δ = 164.16

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(2 CO), 157.12 (CO), 145.44, 145.30, 145.23, 144.95, 144.91, 144.71, 144.17, 144.06, 144.01, 143.69, 141.99, 141.51, 141.31, 140.44, 139.25, 80.60, 70.39, 64.59 (2C, CH_2), 63.56 (1C, CH_2), 29.64 (methylene-C), 14.70 (1C, CH_3), 14.24 (2C, CH_3); UV/Vis (CH_2Cl_2): λ_{max} = 460, 432, 321, 261, 236 nm; MS (EI): m/z = 965 [M^+].

14 (*trans-2*): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.68 (q, J(H,H) = 7 Hz, 2H, CH_2), 4.61 (q, J(H,H) = 7 Hz, 2H, CH_2), 4.53 (q, J(H,H) = 7 Hz, 2H, CH_2), 1.62 (t, J(H,H) = 7 Hz, 3H, CH_3), 1.58 (t, J(H,H) = 7 Hz, 3H, CH_3), 1.50 (t, J(H,H) = 7 Hz, 3H, CH_3); ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): δ = 173.45 (CO), 162.84 (CO), 155.92 (CO), 147.53, 146.59, 146.30, 146.27, 146.00, 145.65, 145.57, 145.54, 145.11, 144.53, 144.37, 144.34, 144.27, 144.13, 144.09, 143.93, 143.70, 143.35, 143.28, 142.95, 142.88, 142.80, 142.66, 142.50, 142.47, 142.28, 142.16, 142.04, 141.80, 141.70, 141.52, 141.36, 140.21, 140.08, 138.70, 138.42, 137.67, 80.97, 77.64, 64.14 (CH_2), 63.17 (CH_2), 63.02 (CH_2), 35.47 (methylene-C), 14.58 (CH_3), 14.22 (CH_3), 14.09 (CH_3); IR (KBr): $\tilde{\nu}$ = 3468, 2977, 2332, 1745, 1462, 1441, 1366, 1226, 1097, 1061, 1025, 864, 753, 738, 704, 673, 587, 573, 553, 542, 527, 496, 473, 441 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 468 (2000), 427 (3000), 402 (4000), 314 (31000), 260 (88000), 240 (88000) nm; MS (EI): m/z = 965 [M^+].

19 (*trans-3*): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.55 (q, J(H,H) = 7 Hz, 2H, CH_2), 4.50 (q, J(H,H) = 7 Hz, 2H, CH_2), 4.45 (q, J(H,H) = 7 Hz, 2H, CH_2), 1.51 (t, J(H,H) = 7 Hz, 3H, CH_3), 1.48 (t, J(H,H) = 7 Hz, 3H, CH_3), 1.42 (t, J(H,H) = 7 Hz, 3H, CH_3); ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): δ = 162.90 (2 CO), 155.79 (CO), 147.09, 147.01, 146.78, 146.73, 146.52, 146.39, 146.32, 146.21, 146.16, 145.85, 145.77, 145.74, 145.71, 145.68, 145.37, 145.16, 144.90, 144.78, 144.51, 144.44, 144.41, 144.38, 144.25, 144.19, 144.00, 143.87, 143.72, 143.63, 143.49, 143.45, 143.32, 143.23, 143.19, 143.09, 142.97, 142.67, 142.52, 142.30, 142.12, 142.03, 141.89, 141.79, 141.23, 140.50, 140.30, 140.06, 139.46, 139.43, 138.49, 81.29, 80.86, 71.75, 71.24, 64.11 (CH_2), 63.12 (CH_2), 63.03 (CH_2), 51.60 (methylene-C), 14.52 (CH_3), 14.14 (CH_3), 14.05 (CH_3); IR (KBr): $\tilde{\nu}$ = 3478, 2978, 2333, 2088, 1745, 1542, 1462, 1430, 1366, 1297, 1231, 1211, 1100, 1061, 1023, 898, 867, 846, 795, 783, 767, 754, 739, 707, 682, 670, 598, 585, 572, 546, 528, 522, 492, 454, 439 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 483 (2000), 421 (2000), 411 (3000), 316 (29000), 247 (97000) nm; MS (EI): m/z = 965 [M^+].

24 (*trans-4*): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.54 (q, J(H,H) = 7 Hz, 2H, CH_2), 4.50 (q, J(H,H) = 7 Hz, 2H, CH_2), 4.47 (q, J(H,H) = 7 Hz, 2H, CH_2), 1.47 (t, J(H,H) = 7 Hz, 3H, CH_3), 1.44 (t, J(H,H) = 7 Hz, 3H, CH_3), 1.42 (t, J(H,H) = 7 Hz, 3H, CH_3); ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): δ = 163.67 (CO), 163.61 (CO), 156.57 (CO), 148.22, 147.12, 146.88, 146.50, 146.44, 146.26, 146.13, 145.81, 145.74, 145.65, 145.52, 145.46, 145.36, 145.34, 145.29, 145.11, 145.07, 144.93, 144.90, 144.52, 144.45, 144.23, 144.08, 143.81, 143.52, 143.45, 143.43, 143.32, 143.05, 143.02, 142.88, 142.58, 142.50, 142.36, 142.30, 142.23, 142.12, 141.85, 141.71, 141.67, 141.24, 141.21, 140.59, 140.41, 140.12, 139.66, 139.13, 138.68, 136.95, 136.44, 80.67, 80.35, 71.29, 70.83, 64.35 (CH_2), 63.36 (CH_2), 63.33 (CH_2), 50.33 (methylene-C), 14.55 (CH_3), 14.14 (CH_3), 14.09 (CH_3); IR (KBr): $\tilde{\nu}$ = 3426, 2979, 1745, 1462, 1367, 1296, 1234, 1095, 1063, 1025, 865, 733, 705, 582, 553, 529, 478, 411 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 452 (2000), 416 (3000), 315 (28000), 248 (77000) nm; MS (EI): m/z = 965 [M^+].

30 (*e'*): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.45 (q, J(H,H) = 7 Hz, 4H, CH_2), 4.43 (q, J(H,H) = 7 Hz, 2H, CH_2), 1.43 (t, J(H,H) = 7 Hz, 6H, CH_3), 1.42 (t, J(H,H) = 7 Hz, 3H, CH_3); ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): δ = 162.92 (2 CO), 155.96 (CO), 147.50, 147.21, 146.72, 145.93, 145.67, 145.52, 144.85, 144.79, 144.67, 144.59, 144.44, 144.38, 144.34, 144.11, 144.06, 143.87, 143.61, 143.41, 143.15, 142.80, 142.55, 141.91, 141.44, 140.17, 138.80, 79.97, 71.49, 70.24, 64.06 (CH_2), 63.10 (2 CH_2), 51.14 (methylene-C), 14.43 (CH_3), 14.06 (2 CH_3); IR (KBr): $\tilde{\nu}$ = 3468, 2979, 2331, 1745, 1462, 1441, 1425, 1366, 1296, 1236, 1212, 1180, 1097, 1062, 1022, 868, 835, 804, 787, 755, 741, 706, 588, 555, 547, 525, 475 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 480 (3000), 421 (3000), 310 (37000), 252 (98000) nm; MS (EI): m/z = 965 [M^+].

31 (*e''*): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.46 (q, J(H,H) = 7 Hz, 2H, CH_2), 4.45 (q, J(H,H) = 7 Hz, 2H, CH_2), 4.42 (q, J(H,H) = 7 Hz, 2H, CH_2), 1.45 (t, J(H,H) = 7 Hz, 6H, CH_3), 1.42 (t, J(H,H) = 7 Hz, 3H, CH_3); ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): δ = 162.50 (CO), 162.42 (CO), 155.28 (CO), 147.00, 146.16, 146.05, 145.78, 145.64, 145.60, 145.54, 145.19, 144.85, 144.72, 144.67, 144.54, 144.44, 144.31, 144.13, 143.74, 143.52, 143.27, 142.92, 142.55, 142.42, 142.31, 141.77, 141.64, 141.19, 139.06, 138.77, 80.74, 79.40, 71.68, 63.85 (CH_2), 62.81 (CH_2), 62.78 (CH_2), 53.07 (methylene-C), 14.48 (CH_3), 14.05 (CH_3), 13.98 (CH_3); IR (KBr): $\tilde{\nu}$ = 3483, 2978, 2933, 2333, 1744, 1543, 1460, 1441, 1424, 1366, 1297, 1233, 1212, 1181, 1129, 1096, 1068, 1023, 978, 865, 842, 801, 776, 766, 758, 745, 737, 706, 671, 655, 592, 571, 560, 553, 542, 528, 503, 484, 446, 432 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 479 (3000), 418 (2000), 407 (3000), 395 (4000), 359 (15000), 308 (43000), 251 (112000) nm; MS (EI): m/z = 965 [M^+].

36 (*cis-3*): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.53–4.40 (m, J(H,H) = 7 Hz, 9H, CH_2), 1.43 (t, J(H,H) = 7 Hz, 6H, CH_3), 1.42 (t, J(H,H) = 7 Hz, 3H, CH_3); UV/Vis (CH_2Cl_2): λ_{max} = 454, 419, 318, 254 nm; MS (EI): m/z = 965 [M^+].

41 (*cis-2*): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.54–4.38 (m, J(H,H) = 7 Hz, 9H, CH_2), 1.47 (t, J(H,H) = 7 Hz, 3H, CH_3), 1.42 (t, J(H,H) = 7 Hz, 3H, CH_3), 1.38 (t, J(H,H) = 7 Hz, 3H, CH_3); UV/Vis (CH_2Cl_2): λ_{max} = 463, 433, 408, 317, 258 nm; MS (EI): m/z = 965 [M^+].

42 (*cis-1*): ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.57–4.26 (m, J(H,H) = 7 Hz, 6H, CH_2), 1.53 (t, J(H,H) = 7 Hz, 3H, CH_3), 1.40 (t, J(H,H) = 7 Hz, 3H, CH_3), 1.39 (t, J(H,H) = 7 Hz, 3H, CH_3); ^{13}C NMR (100.5 MHz, $CDCl_3$, 25 °C): δ = 161.53 (CO), 161.05 (CO), 154.30 (CO), 150.21, 148.57, 147.03, 146.83, 146.69, 146.54, 145.69, 145.63, 145.45, 145.42, 145.26, 145.08, 145.01, 144.92, 144.73, 144.56, 144.46, 144.15, 143.85, 143.79, 143.62, 143.56, 143.37, 143.31, 143.27, 143.15, 143.06, 143.01, 142.68, 142.41, 142.35, 142.13, 141.83, 141.72, 141.70, 141.42, 141.39, 141.34, 140.92, 140.84, 140.26, 140.23, 139.90, 139.51, 139.41, 139.25, 139.03, 138.55, 73.40, 68.02, 66.58, 63.46 (CH_2), 62.43 (CH_2), 62.32 (CH_2), 58.30, 52.20 (methylene), 14.41 (CH_3), 14.03 (CH_3), 13.79 (CH_3); IR (KBr): $\tilde{\nu}$ = 3447, 2979, 1747, 1396, 1233, 1181, 1097, 1061, 1023, 858, 758, 742, 703, 588, 547, 529, 496 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 464 (2000), 425 (3000), 327 (29000), 257 (109000) nm; MS (EI): m/z = 965 [M^+].

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