Opening and Closure of the Fullerene Cage in *cis-1*-Bisimino Adducts of C_{60}: The Influence of the Addition Pattern and the Addend

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Dedicated to Professor Friedrich Hund on the occasion of his 100th birthday

Abstract: The synthesis, isolation, and spectroscopic characterization of the bisimino[60]fullerenes $C_{60}(NCOOR)_2$ (**1a**: R = Et, **1b**. R = *t*Bu) with a *cis-1* addition pattern as well as of their regioisomeric analogues **2**–**7** with different addition patterns are described. Whereas compounds **2**–**7** are typical fulleroaziridines and obey the rule of the minimization of [5,6] double bonds, the *cis-1* isomers **1a** and **1b** represent the first examples of fullerene derivatives with open transannular [6,6] bonds. Characteristic features within the fullerene framework of these valence isomers **VI** are the presence of a doubly bridged open 14-membered ring with a phenanthrene perimeter as well as of an 8-membered 1,4-diazocine heterocycle. Moreover, it is shown that, by transforming *cis-1*-C60(NCOO*t*Bu)2 (**1b**) into *cis-1*-C60(NH)2 (**1c**), the fullerene cage can be closed in an intraring $2\pi \rightarrow 2\sigma$ isomerization to valence isomer **V**. These are the first chemical modifications of the fullerene core that allow the synthesis of both open and closed valence isomers with the same addition pattern. Density-functional as well as AM1 calculations corroborate the experimental findings that it depends on the addition pattern as well as on the nature of the addends whether or not the transannular [6,6] bonds are closed. Only in the *cis-1* adducts $C_{60}(NR)_2$ that prefer planar imino bridges (e.g., carbamates or amides) are the open forms **VI** more stable than the closed isomers **V**.

Keywords
clusters · fullerenes · nitrenes · regioselectivity · valence isomerization

Introduction

Among the cycloadducts of C_{60}[1] the methano and imino derivatives[1–13] are a special case, since the addend can bridge not only junctions between two six-membered rings but also junctions between five- and a six-membered rings. The resulting constitutional isomers are denoted as [6,6] and [5,6] adducts.[1–13] Without considering the specific properties of the fullerene moiety[1] and using the analogy of the methano- and iminoannulenes,[14] we can envisage that the [6,6] and [5,6] transannular bonds can, for example, depending on the addend, either be open or closed. This leads to four possible isomers of monoaddition products, namely, open and closed [6,6], and open and closed [5,6] adducts (**I**–**IV**, Fig. 1). So far, only the closed [6,6]-bridged adducts **I** and the open [5,6]-bridged adducts **III** have been found. Computational investigations[15] confirm the experimental finding[1–13] that **I** and **III** are the most stable isomers.

In order to understand this behavior the following structure-related aspects of the [60]fullerene molecule[1] have to be considered: Owing to the spherical framework, the sp^2-C atoms of C_{60} are highly pyramidalized, causing a large amount of strain energy, which makes up about 80% of the heat of formation.[16] The most efficient relief of strain determines the structure of fullerenes and is one of the major driving forces for the regioselectivity of their addition reactions.[1] The energetically most favorable and experimentally observed arrangement within the [60]fullerene framework involves alternating bond lengths, with shorter [6,6] bonds and longer [5,6] bonds.[1] As a consequence, of the 12500 possible Kekulé structures of C_{60}, that with the lowest energy contains exclusively [6,6] double bonds and [5,6] single bonds. Therefore, C_{60} can be considered as a sphere built up of fused [5]radialene and cyclohexatriene units. These structural features are also present in fullerene derivatives. The analysis of a variety of single-crystal structures of 1,2-cycloadducts of C_{60} (cycloaddition to a [6,6] double bond), for example, reveals that the [5]radialene-type pattern is preserved.[17] Based on these and other observations the following rule of reactivity[1–3] can be

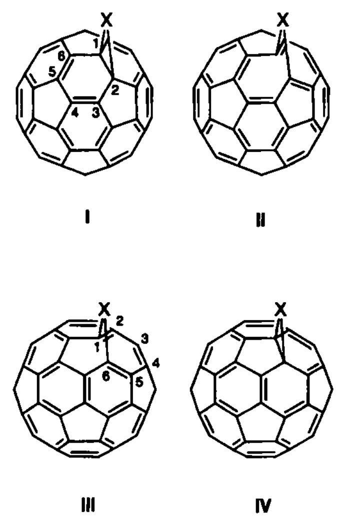

Fig. 1. Different constitutional and valence isomers **I**–**IV** of monomethano[60]fullerenes (X = CRR') and monoimino[60]fullerenes (X = NR).

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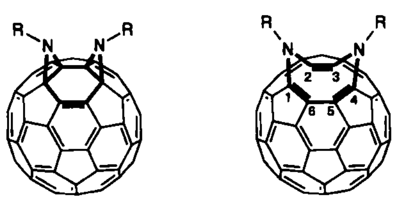
deduced for [60]fullerene: *The regiochemistry of addition reactions is governed by the drive to minimize the number of [5,6] double bonds.* Consistent with this rule is the fact that monomethano- and monoimino[60]fullerenes are found as the isomers **I** or **III**, which lack the energetically unfavorable [5,6] double bonds,[18] whereas the hypothetical structures **II** and **IV** contain three and two [5,6] double bonds, respectively (Fig. 1). Systematic PM3 calculations[15b] on a series of methanofullerenes $C_{61}R_2$ predicted the structures **I** and **III** to be 14–22 $kcal\,mol^{-1}$ more stable than the closed [5,6] isomer **IV**, and no minimum was observed for the [6,6] open structure **II**. The isolation of closed [5,6]-bridged iminofullerenes has been claimed recently,[11] but shortly thereafter it was proven[13] that the assignment was incorrect and that in fact the open [5,6] structures had been formed. Hence, for monoadducts the case is clear: the formation of open [6,6] and closed [5,6] structures is avoided. What happens upon going to higher addition products? Could the picture be changed if, for example, additional constraints forced by a specific addition pattern are present?

A variety of oligoadducts, for example with two imino[19] and up to six methano bridges,[20] have already been synthesized. In each case, "regular" behavior was observed, that is, either open [5,6]-bridged or closed [6,6]-bridged arrangements were formed. A hint of a new situation was given in our recent report on the green bisimino[60]fullerenes *cis-1*-$C_{60}(NR)_2$ (**1**) (R = COOEt, COO*t*Bu), which are the first examples of bisadducts of C_{60} with organic addends and a *cis-1* addition pattern (Fig. 2, Fig. 3).[21] These iminofullerenes efficiently fragment to give the



V **VI**

Fig. 2. Valence isomers of *cis-1* bisimino[60]fullerenes with closed (**V**) and open (**VI**) transannular [6,6] bonds.

heterofullerene ion $C_{59}N^+$ under FAB-MS conditions.[21] In **1** two [6,6] junctions within the same six-membered ring are bridged by the addends (Fig. 2). The unusual spectroscopic properties led us to the conclusion that the two transannular [6,6] bonds exhibit open character. In this paper we present comprehensive experimental and computational investigations on **1**, its regioisomeric analogues **2**–**8**, other bisimino[60]fullerenes with *cis-1* addition pattern, and monoimino[60]fullerenes. We demonstrate that additional stereoelectronic factors, namely, i) the influence of the *cis-1* addition pattern and ii) the nature of the addend interfere with the principle of the minimization of [5,6] double bonds. In the case of compounds **1a,b**, factors leading to bond opening prevail. These compounds represent the *first examples* of [60]fullerene derivatives with open transannular [6,6] bonds (valence isomer **VI**) (Fig. 2). Characteristic features within the fullerene framework of these valence isomers **VI** are the presence of i) a doubly bridged open 14-membered ring with a phenanthrene perimeter and ii) an 8-membered 1,4-diazocine heterocycle. Upon changing the addition pattern, "regular" behavior with closed transannular [6,6] bonds is observed, as demonstrated by the investigation of the other possible regioisomers of $C_{60}(NCOOEt)_2$. Moreover, we show that, by transforming *cis-1*-$C_{60}(NCOO\textit{t}Bu)_2$ (**1b**) into

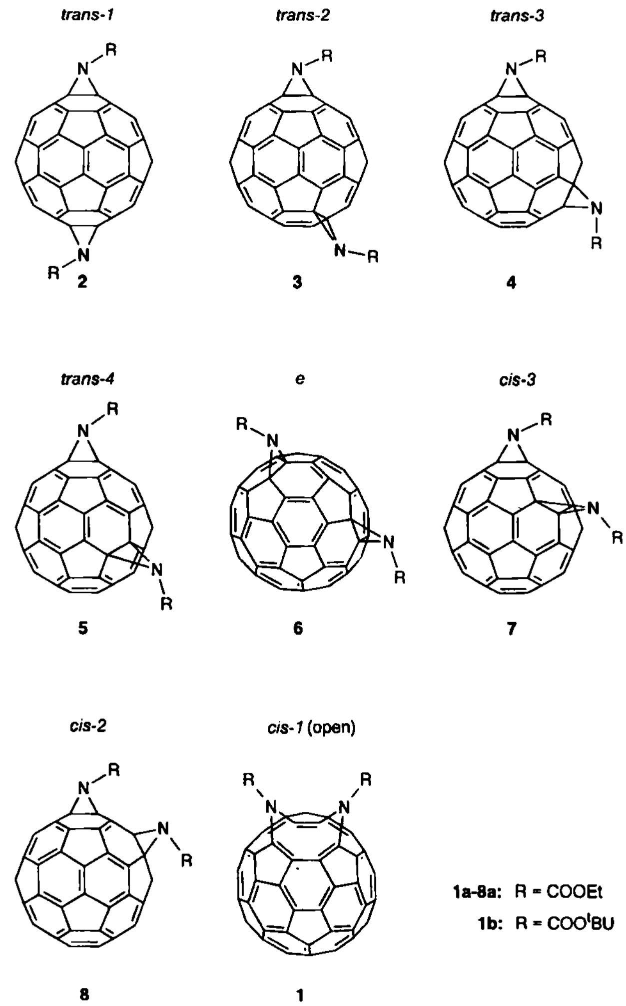


Fig. 3. Eight possible regioisomers of $C_{60}(NCOOEt)$ (**1a**–**8a**) and *cis-1*-$C_{60}(NCOO\textit{t}Bu)_2$ (**1b**).

cis-1-$C_{60}(NH)_2$ (**1c**), the fullerene cage (Fig. 2) can be closed in an intraring Diels–Alder reaction ($2\pi \rightarrow 2\sigma$ isomerization[22]) to valence isomer **V** (Fig. 2). This phenomenon clearly reveals the role of the addend. These are the first chemical modifications of the fullerene core that allow the synthesis of open and closed valence isomers with the same addition pattern.

Results and Discussion

The synthesis of iminofullerenes can either be achieved by the addition of nitrenes or by [3+2] cycloadditions of azides followed by N_2 extrusion from the initially formed triazolines.[4–13, 19] The mechanism of the latter pathway has been proven by the isolation and characterization of a variety of triazolines.[19a, 23] The addition of nitrenes to C_{60} leads predominantly to the closed [6,6]-bridged isomers, whereas the major products formed by the thermal degradation of triazolines are the open [5,6]-bridged isomers, formed as a result of the efficient radical recombination within the intermediate diradical species at C-6.[24] The corresponding other isomer is the by-product in each case. Depending on the conditions, the reaction of C_{60} with azidoformates can proceed in both ways. Addition of azidoformate to a solution of C_{60} in 1,1,2,2-tetrachloroethane or 1-chloronaphthalene at 140–160 °C, for example, leads to the attack by the stabilized nitrenes ROOCN to give predominantly [6,6]-bridged $C_{60}(NCOOR)$ (**9**).[13] On the other hand, by allow-

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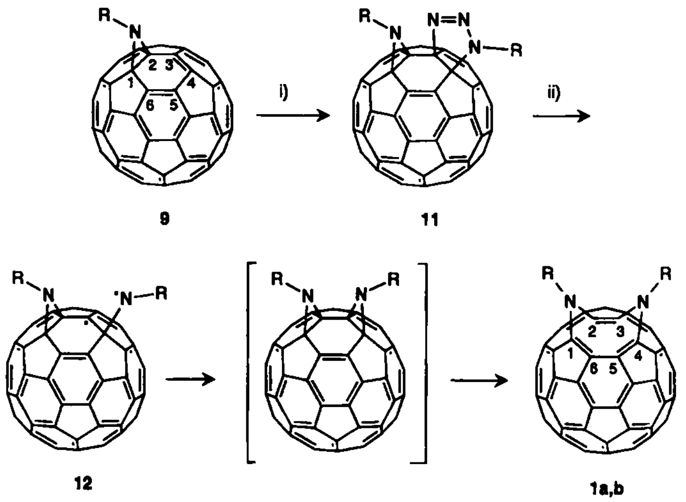
ing a concentrated solution of C_{60} in 1-chloronaphthalene to react with N_3COOR at 60 °C ([3+2] cycloaddition), then adding the tenfold volume of toluene, and heating the reaction mixture to reflux (N_2 extrusion), the corresponding [5,6]-bridged isomers **10** are formed as major products.

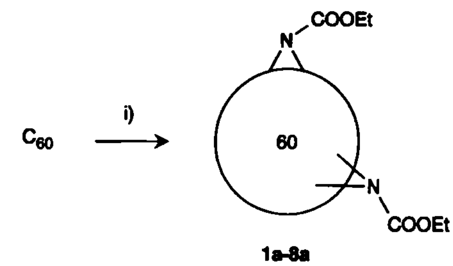
A comparatively regioselective synthesis of **1** can be achieved starting from **9** (Scheme 1). Although the conditions used are



Scheme 1. Reaction conditions and proposed mechanism for the synthesis of **1a** (R = COOEt) and **1b** (R = COO*t*Bu) following the "triazoline route": i) 2 equiv N_3COOR, 1-chloronaphthalene, 60 °C, 4 d; ii) toluene, reflux, 30 min.

those for the synthesis of [5,6] derivatives via intermediate triazolines, of the large number of regioisomeric bisadducts (doubly [6,6]-bridged as well as mixed [6,6]-/[5,6]-bridged isomers), the most polar isomers **1** are formed as major products (>50% yield) relative to other bisadducts. In addition to a directing effect towards the *cis-1* positions by the first addend, which will be discussed below, we explain this result with a mechanism (Scheme 1) based on the AM1-calculated bond polarizations of the starting materials. The reaction intermediate leading to **1** is the mixed triazoline/iminofullerene **11**, formed in a [3+2] cycloaddition, where the negatively polarized nitrogen ($R\text{-}N\text{-}N_2$) of the azide group forms a bond with the positively polarized C atom (e.g. C-4) of a *cis-1* bond. The thermal extrusion of N_2 leads to the diradical intermediate **12**. Because of the location of the first addend in the same six-membered ring, the usual delocalization of spin density within this ring (e.g., by transfer of spin density to C-5) is impossible and radical recombination can only take place at C-3. Hence, the formation of a heterotropylidene-like structure (1,2,4,5-bisimino[60]fullerene) is suppressed. Obviously, a possible spin delocalization in **12** over the 4,3,13,15,16,17-six-membered ring either does not occur or does not account for the hypothetical formation of a [5,6] open structure with 4,17-bridging. An intraring retro-Diels–Alder reaction ($2\pi \rightarrow 2\sigma$ isomerization) leads to ring opening of the non-isolable closed form **V** to give **1**. An analogous ring opening reaction was observed by Prinzbach[22, 25] and Vogel[26] during the synthesis of 1,4-dihydro-1,4-diazocine derivatives.

For the comparison of spectroscopic properties we were interested in the characterization of the regioisomeric analogues **2a**–**8a** (Fig. 3). In order to avoid formation of mixed [5,6]/[6,6] bisadducts as far as possible, we used the direct thermal treatment of **9a** with two equivalents of ethyl azidoformate at 145 °C in 1,1,2,2-tetrachloroethane, which are the conditions for preferred nitrene additions to [6,6] double bonds[13] (Scheme 2).



Scheme 2. Synthesis of **1a**–**8a** by the nitrene route. i) TCE reflux, 1.5 equiv N_3COOEt, 20 min.

Mixed [5,6]/[6,6] adducts were formed only in traces, as more polar fractions eluting with retention times similar to the *cis-2* adduct **8a**. Hence, it is straightforward to isolate the *trans*, *e* (equatorial), and *cis-3* adducts **2a**–**7a** as well as the most polar bisadduct **1a** by preparative HPLC (silica gel, toluene/hexane 8:2). The *cis-2* adduct **8a**, however, elutes simultaneously with a mixed [5,6]/[6,6] bisadduct and could not be obtained in pure form. The order of elution (Table 1) of the bisadducts **1**–**8** cor-

Table 1. Order of elution (no.), symmetry, relative yield, and assignment of the bisadducts **1a**–**8a** formed by thermal treatment of C_{60} with ethyl azidoformate (direct addition of nitrenes)

No.	Compd	Symmetry [a]	Rel. yield [%]	Assignment [b]
1	**2a**	D_{2h}	3.1	*trans-1*
2	**3a**	C_2	13.0	*trans-2*
3	**4a**	C_2	11.9	*trans-3*
4	**5a**	C_s	10.6	*trans-4*
5	**6a**	C_s	26.9	*e*
6	**7a**	C_2	11.8	*cis-3*
7	**8a**	C_s	1.6 [c]	*cis-2*
8	**1a**	C_s	21.0	*cis-1*

[a] Determined from ^1H and ^{13}C NMR spectra. [b] Based on the symmetry, the order of elution (increasing polarity), and the comparison of the UV/Vis spectra with those of the corresponding isomers of $C_{62}(COOEt)_4$ [20a]. [c] Yield estimated as upper limit since **8a** was not isolated in pure form.

responds to the expected polarity and is the same as that observed for the $C_{62}(COOEt)_4$ analogues formed upon twofold cyclopropanation of C_{60} with diethyl bromomalonate.[20a] The two reactions show similar trends, such as the preferred formation of *e* adducts, although the regioselectivity of the twofold nitrene addition is less pronounced since more drastic reaction conditions are required here (145 °C vs. room temperature[20a]). The major difference between the two reactions is that the *cis-1* adduct of $C_{60}(NCOOEt)_4$ (**1a**) is the second most abundant regioisomer, in contrast to the $C_{62}(COOEt)_4$ series, where the *cis-1* adduct was not formed because of steric repulsion between the malonate addends. The absence of steric repulsion between the two imino addends in **1a** (Table 2) indicates that an attack

Table 2. AM1-calculated stabilities ($AM1_{HOF}$) of the eight isomers of $C_{60}(NCOOMe)_2$ with closed and open transannular [6,6] bonds.

Position	$AM1_{HOF}$ (closed) [kcal mol^{-1}]	$AM1_{HOF}$ (open) [kcal mol^{-1}]
trans-1	866.85	884.74
trans-2	866.92	883.80
trans-3	866.73	883.98
trans-4	866.80	886.56
e	866.64	882.52
cis-3	868.39	884.68
cis-2	869.13	892.56
cis-1	865.45	862.45

at a *cis-1* position is in principle the regioselectively preferred process. This becomes understandable if one considers the electronic and geometric situation in a [6,6]-bridged monoadduct of C_{60}. Apart from the e'' double bonds (Fig. 4), the *cis-1* double

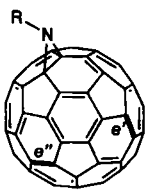


Fig. 4. Two different types of *e* bonds in a 1,2-monoadduct of C_{60}. Bisadducts formed by addition to e' or e'' positions are identical if both addends are identical and symmetrical (e.g., two CR_2 or NR bridges).

bonds are the significantly shorter than any others in the molecule, almost independently of the nature of the first addend, as shown by AM1 calculations[20b, 27] as well as by analysis of a variety of single crystal structures.[17] This characteristic distortion of the cage geometry caused by the binding of the first addend has direct consequences for the coefficients of frontier orbitals in the corresponding positions. The highest coefficients in the HOMO, for example, are located at *cis-1* and e″ positions;[20b] as a result addition of nitrenes at these positions is favored, exactly as observed (Table 1). In these nitrene additions, no steric effects interfere, and only the directing effects of the fullerene core itself, which is characteristically distorted by the attachment of the first addend, are responsible for the observed regioselectivities.

We previously mentioned the remarkable spectroscopic properties of **1**,[21] especially the unusual ^{13}C NMR chemical shifts of the bridgehead carbons C-2 and C-3 at $\delta = 114$ and C-1 and C-4 at $\delta = 128$. This spectroscopic behavior led us to the assumption that compounds **1** might exhibit [6,6] bond character. With the present comparative study, we demonstrate, based on comprehensive experimental and theoretical material, that compounds **1** are indeed the first fullerene derivatives with open transannular [6,6] bonds.

The monoadducts **9** as well as the bisadducts **2a**–**7a** show the expected NMR spectroscopic behavior for closed [6,6] structures[5–7, 9–13] (Fig. 5). In the monoadducts **9** the resonances of the bridgehead carbons C-1 and C-2 appear in the sp^3 region at $\delta = 80$, which is typical for an sp^3 fullerene C atom attached to an imino bridge.[13] The structural assignment of the bisadducts **2a**–**7a** (Table 1) is based on i) their ^1H and ^{13}C NMR spectra from which their symmetry (D_{2h}, C_s or C_2) can be deduced, ii) comparison of their polarity[20a] with the order of elution, and iii) comparison of their UV/Vis spectra with those of the series $C_{62}(COOEt)_4$.[20a] For the unambiguous structural assignment of the *trans-1* and *e* isomers **2a** and **6a** NMR spectroscopy alone is sufficient, since **2a** is the only isomer with D_{2h} symmetry and **6a** is the only C_s symmetrical isomer in which the imino bridges are located in the mirror plane. Hence, in the ^1H NMR spectrum of **6a** there are two quartets and two triplets corresponding to the two different ethyl groups, whereas in all other bisadducts the ethyl groups are magnetically equivalent. Moreover, in contrast to all the other C_s- or C_2-symmetric bisadducts (**1a**, **3a**–**5a**, **7a**, and **8a**), which each have two different types of bridgehead C atoms, three are present in **6a**. In the ^{13}C NMR spectrum of **6a** the corresponding three signals appear at $\delta = 80.9$, 80.4, and 79.6 (Fig. 5). The order of elution for isomers **2a** and **6a** is as expected considering their polarity (Table 1). The most important result to come out from the analysis of the NMR spectra of **2a**–**7a** is that all bridgehead C atoms clearly resonate in the sp^3 region at $\delta = 79$–87 (Fig. 5). This reveals "regular" behavior with closed transannular [6,6] bonds.

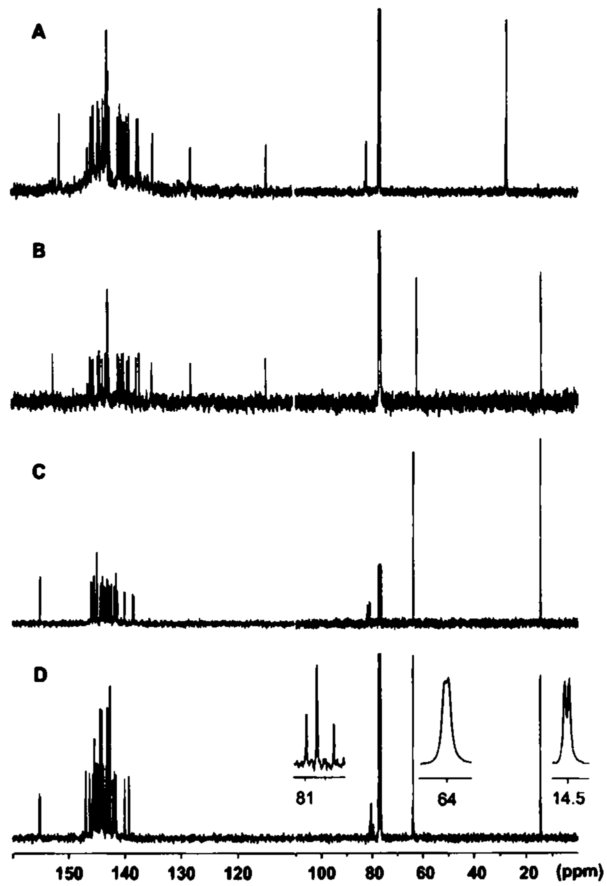


Fig. 5. ^{13}C NMR spectra of A) **1b**, B) **1a**, C) **4a** (*trans-3* isomer), and D) **6a** (*e* isomer). The insets in D) show the signals for the three magnetically different sp^3 bridgehead C atoms ($\delta = 81$), as well as for the two different methylene ($\delta = 64$) and methyl groups ($\delta = 14$) of **6a**.

^{13}C NMR investigations on **1a,b** (Fig. 5), $^{15}N,^{15}N$-**1a**, with both imino bridges ^{15}N-labeled,[21] and $^{14}N,^{15}N$-**1a**, with one ^{15}N-labeled imino bridge,[21] clearly prove that the transannular [6,6] bonds are open. With the exception of the signals for ester groups, the spectra of **1a** and **1b** are essentially the same. The C_s symmetry is reflected by 32 signals for the fullerene C atoms; four of these are of half intensity and correspond to the C atoms located in the mirror plane at $\delta = 146.5$, 144.4, 140.8, and 139.2 for **1a** and at $\delta = 146.4$, 144.3, 140.4, and 139.5 for **1b**. The bond connectivities within the six-membered ring carrying the imino bridges can be deduced from the data of $^{15}N,^{15}N$-**1a** and $^{14}N,^{15}N$-**1a**[21]. In $^{15}N,^{15}N$-**1a** the signals at $\delta = 128$ and 114 split, respectively, into a doublet with $^1J(C,N) = 14$ Hz and a doublet of doublets with $^1J(C,N) = 15$ and $^2J(C,N) = 3$ Hz. This proves that i) the corresponding C atoms of the fullerene core are directly attached to the imino-bridges and ii) that a 1,2,3,4-addition pattern (*cis-1* adduct) must be present. The only other structure that in principle would fulfil the same requirements is a 2,3,4,5-adduct. However, this can be ruled out from the fact that **9** with a preexisting 1,2-pattern is the precursor for **1**. The three additional signals with $^2J(C,^{15}N)$ couplings required for a *cis-1* addition pattern are found at $\delta = 139.31$ ($^2J(C,N) = 2$ Hz), 137.18 ($^2J(C,N) = 1$ Hz), and 134.92 ($^2J(C,N) = 3$ Hz). As expected, the signal for C-2 and C-3 at $\delta = 114.73$ in $^{14}N,^{15}N$-**1a** splits into a large doublet with $^1J(C,N) = 15$ Hz and a small doublet with $^2J(C,N) = 3$ Hz, whereas the signal for C-1 and C-4 at $\delta = 128.09$ splits into a singlet and a doublet with $^1J(C,N) = 14$ Hz.

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The chemical shifts of the bridgehead carbons C-1, C-2, C-3, and C-4 in the ^{13}C NMR spectra of **1** are comparable to similar doubly bridged systems like 1,4-dimethoxycarbonyl-1,4-diazocine[26] (**13**), bismethano[14]annulene with a phenanthrene perimeter[28,29] (**14**), and bisimino[14]annulenes with an anthracene perimeter[28,30] (**15**) (Fig. 6). Especially the almost

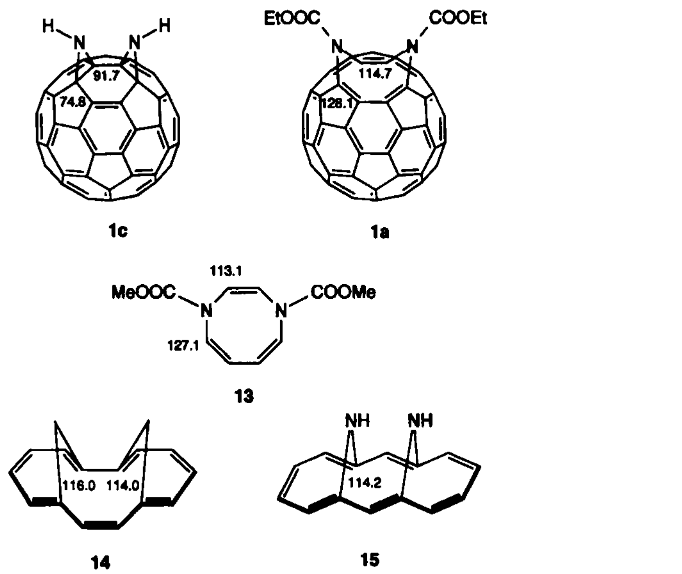


Fig. 6. Comparison of the ^{13}C NMR data for the bridgehead C atoms of **1c**, **1a**, **14** [28,29], and **15** [28,30] and the ring C atoms bound to the N atoms in **13** [26].

identical data of **1a,b** and **13** reflect the presence of a 1,4-diazocine perimeter in the framework of the open fullerenes **1a,b**. Compared to typical chemicals shifts of sp^2 [60]fullerene C atoms (δ between 150 and 130), the signals for C-1, C-2, C-3, and C-4 appear to be shifted somewhat upfield. This is probably due to the specific substructure of the diazocine ring in **1** as well as to the influence of the N atoms attached to the sp^2 C atoms of the fullerene cage, since in [5,6]-bridged monoimino[60]fullerenes like **10**, C-1 and C-6 carrying the imino bridge resonate upfield ($\delta = 134$) of all other sp^2 C atoms of the fullerene cage, as has been shown by using ^{15}N-labeled material and determining the C–N couplings.[13]

Variable-temperature ^{13}C NMR investigations on **1a** showed no change in the chemical shift of C-1, C-2, C-3, and C-4 down to $-60\,°C$. Upon further lowering of the temperature the three possible conformers, two with parallel and one with an antiparallel carbonyl arrangement, finally freeze out with a coalescence at about $-60\,°C$. The resonances of the C atoms located in the neighborhood of the N-COOEt groups also split into three resolved signals. For example, the presence of the three frozen out conformers at $-100\,°C$ lead to three resonances for C-2 and C-3 ($\delta = 128.47$, 128.31, 126.26) and three for C-1 and C-4 ($\delta = 115.66$, 114.67, 113.15). Hence, since there is no change in peak position for the bridgehead C atoms in **1** upon lowering the temperature down to $-60\,°C$, the coalescence and peak splitting is due to hindered rotation of the side chains (amide bonds); this is also reflected in the absence of signals for bridgehead C atoms in the sp^3 region. An equilibrium between valence isomers **V** and **VI** can thus be ruled out, and **VI** is the stable structure of **1**.

The open transannular bonds in **1** have a significant influence on its electronic properties, as can be seen by comparison with the properties of the closed isomers **2a–7a**. Whereas the closed bisadducts **2a–7a** exhibit characteristic reddish colors in solution, the doubly ring opened isomers **1** are green. Each isomer **2a–7a** shows a specific red tone ranging from copper red to red-orange. The color depends predominantly on the addition pattern rather than on the nature of the first addend. This is clearly reflected by the similarity of the red tones in **2a–7a** and in the corresponding isomers of the $C_{62}(COOEt)_4$ series.[20a] Hence, the UV/Vis spectra of these two series of regioisomers are essentially the same. Very characteristic for each addition pattern is the structure of the 400–700 nm region in each spectrum (Fig. 7). Significantly, the absorption band of **1a** and **1b**

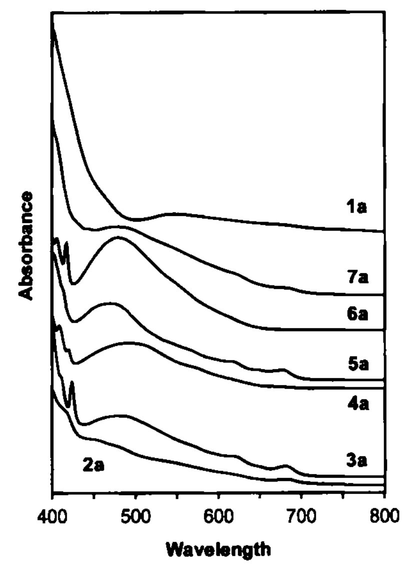


Fig.7. UV/Vis spectra (CH_2Cl_2) of the bisadducts **1a–7a**.

in CH_2Cl_2 at $\lambda_{max} = 338$ nm appears with a bathochromic shift of about 20 nm compared to the corresponding bands of **2a–7a** with λ_{max} values at about 317 nm. In addition, these absorptions of **1a** and **1b** exhibit solvatochromic behavior. For example, using toluene as solvent leads to a further bathochromic shift to $\lambda_{max} = 346$ nm (Fig. 8). To our knowledge there are no other [60]fullerene derivatives with comparatively high λ_{max} values for these absorptions.

In order to investigate whether the ring opening in **1** depends not only on the addition pattern but also on the nature of the addend, we carried out modifications in the side chain of **1** to see if this would lead to a reclosure of the transannular [6,6] bonds

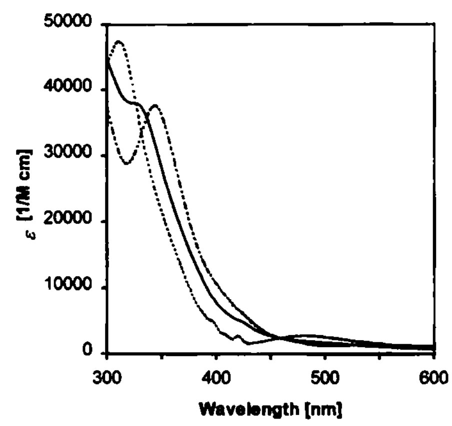
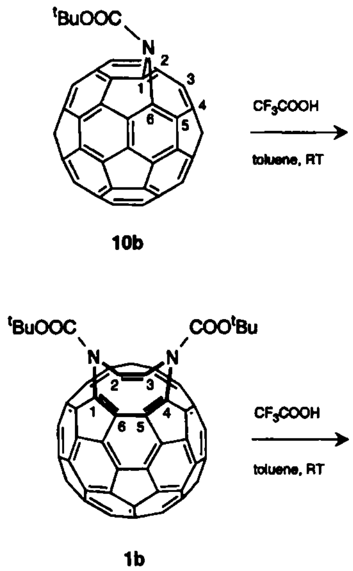


Fig. 8. UV/Vis spectra (toluene) of the bisadducts **6a** (---), **1b** (····), and **1c** (—).

in an intramolecular Diels–Alder reaction ($2\pi \rightarrow 2\sigma$ isomerization). The best candidate for such an addend modification is **1b**, since the Boc groups bound to the imino bridge should be readily removed by treatment with acids. Spontaneous decarboxylation of the intermediate carbamic acid should then lead to the NH analogue $C_{60}(NH)_2$ (**1c**). Similar transformations, such as the thermal treatment of **9b** in boiling tetrachloroethane or its decomposition on alumina, have already been used to synthesize the parent fulleroaziridine 1,2-$C_{60}NH$ (**9c**). However, these methods were not successful for the synthesis of **1c**, since most of the material decomposed or did not elute from alumina columns. Hence, we looked for milder conditions by trying out several methods using first the [5,6] open isomer 1,6-C_{60}NCOO*t*Bu **10b** as test substance,[13] since it is more readily available than **1b**. The best method for the conversion of the Boc derivatives **1b** and **10b** into their NH analogues **1c** and **10c** turned out to be treatment with trifluoroacetic acid in toluene at room temperature (Scheme 3). This reaction proceeds in quantitative yield. In this way the parent [5,6]-bridged 1,6-C_{60}(NH) (**10c**) was synthesized for the first time along with *cis-1*-$C_{60}(NH)_2$ (**1c**). The parent *cis-1* derivative **1c** has *closed* transannular [6,6] bonds.



Scheme 3.

In contrast to **1a,b** the color of **1c** in solution is red-orange, suggesting significantly different electronic structures. This is reflected in the electronic absorption spectra of **1b** and **1c** especially in the visible range (Fig. 8). UV/Vis spectroscopy can be used for monitoring the conversion from **1b** to **1c**. During the reaction, which proceeds within a period of 20 hours, quasi-isosbestic points develop; this demonstrates that the conversion to **1c** proceeds stepwise, presumably through the removal of one protecting group, followed by a second deprotection coupled to an intramolecular Diels–Alder reaction. In the ^{13}C NMR spectrum of **1c** the bridgehead C atoms C-2/C-3 and C-1/C-4 resonate at $\delta = 91.7$ and 74.7, respectively (Fig. 6); this clearly shows that, in analogy to **2–7** and **9**, the bridgehead C atoms are sp^3-hybridized and thus the transannular [6,6] bonds are closed.

Computational investigations confirm the experimental findings that the transannular [6,6] bonds in **1** are open and those in **2–8** closed. A comparison of the AM1 stabilities[31, 32, 33] of the eight regioisomers of $C_{60}(NCOOMe)_2$ reveals that, with the exception of the *cis-1* adduct, the valence isomers with closed transannular [6,6] bonds are at least 14 kcal mol^{-1} more stable than the ring-open forms (Table 2). This is the expected result considering the principle of the minimization of energetically unfavorable [5,6] double bonds: in the open valence isomers of **2–8** six [5,6] double bonds would be required. On the other hand, the AM1 heat of formation of the *cis-1* open structure **VI** is 3 kcal mol^{-1} lower than that of the closed form **V** (Table 2, Fig. 2). Interestingly, even the unfavorable closed structure **V** of the *cis-1* isomer is more stable than those of all other regioisomers. PM3, force field (MM2), and density-functional calculations reveal similar trends in stability. For comparison, AM1 and density-functional calculations are listed in Table 3. In order to reduce the CPU times to a reasonable scale, density-functional calculations were carried out for the free acid $C_{60}(NCOOH)_2$. The open valence isomer **VI** of *cis-1*-$C_{60}(NCOOH)_2$ is more stable than the closed form by about 23 kcal mol^{-1} using the 3-21G basis set with the Becke/Lee-Yang-Paar (BLYP) functional[34, 35] (Table 3). Only a plateau on the energy surface was found for the closed form **V** of *cis-1*-$C_{60}(NCOOH)_2$. The energy difference between the closed and the open form is less pronounced, but still significant ($\Delta\Delta H_f = 6.76$) upon going to a higher-level basis set (BLYP/D59*,5D) and performing a single-point calculation using the BLYP/3-21G-minimized geometry. The experimental results of **1a–c** showed that, next to the addition pattern, it is the nature of the imino addend that determines whether a *cis-1* adduct has closed or open transannular [6,6] bonds. For carbamates or amides density-functional and semiempirical AM1 calculations (Table 3) predict the open forms to be more stable than the closed forms, whereas the opposite is the case for imino addends with alkyl chains. Of interest are the results for $C_{60}(NH_2)_2^{2+}$ and $C_{60}N_2^{2-}$. The former prefers the closed and the latter the open structure with a large energy difference. However, in contrast to the experimental results, AM1 predicts the closed valence isomer of **1c** to be slightly more stable than the open form (Table 3); this clearly demonstrates the limitations of such semiempirical methods, especially when such a complex balance of stereoelectronic factors is considered. The two imino N atoms in the BLYP/3-21G-calculated structure of open *cis-1*-$C_{60}(NCOOH)_2$ (Fig. 9) are almost planar (amide or carbamate character); this arrangement allows the free electron pairs of these N atoms to participate in the conjugation with the carboxylic groups as well as to a small extent with the π-electron system of the diazocine perimeter. The shortest bond within the 1,4-diazocine perimeter is the [5,6] bond between C-2 and C-3

Table 3. Calculated differences in the heats of formation of closed and open *cis-1*-$C_{60}(NR)_2$ derivatives

Addend	Method	ΔH_f(closed) – ΔH_f(open) [kcal mol^{-1}]
NCOOH	BLYP/3-21G	23.43
NCOOH	BLYP/D59*,5D [a]	6.76
NCOOH	AM1	3.57
NCOOMe	AM1	3.00
NCOOEt	AM1	3.28
NCOME	AM1	4.95
NMe	AM1	–3.17
NEt	AM1	–3.23
NH	AM1	2.38
NH_2^+	AM1	–3.65
N^-	AM1	17.94

[a] Single point calculation based on the BLYP/3-21G-minimized geometry.

0947-6539/96/0208-0940 $ 15.00+.25/0

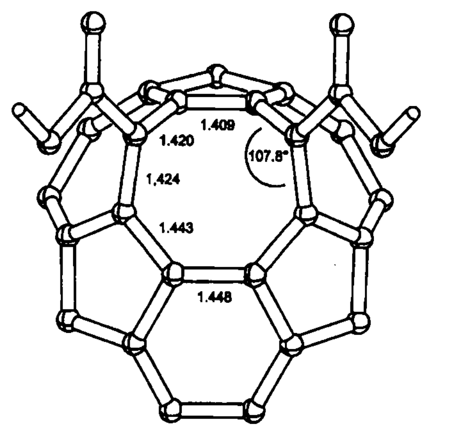


Fig. 9. Representation of selected bond lengths and angles within the diazocine moiety of the BLYP/3-21G-calculated structure of *cis-1*-$C_{60}(NCOOH)_2$. The rest of the fullerene cage is omitted for clarity.

with a length of 1.409 Å, which is significantly shorter than the undisturbed [5,6] bonds of [60]fullerenes (ca. 1.45 Å).[1] Interestingly, the BLYP/3-21G bond lengths between C-4 and C-5, C-5 and C-6, and C-6 and C-1 are almost the same and are similar to those of normal [5,6] bonds; this reflects the fact that the double bond character is significantly less than that of regular [6,6] double bonds, which exhibit bond lengths of about 1.38 Å . The distance between the bridgehead C atoms C-1 and C-2 as well as C-3 and C-4 is 2.298 Å. The AM1 coefficients in the HOMO-1 of **1a** are highest by a significant margin at the [5,6] bonds between C-2 and C-3 and that of the HOMO are highest at the [5,6] bonds C-4 and C-5 as well as at C-1 and C-6. Hence, these positions should be the most reactive sites within **1a,b**. Significantly, in all calculated open structures $C_{60}(NR)_2$ (R = COOR', COR', Table 2, Table 3), independently of the method used, the N atoms of the imino bridges are planar, whereas in all closed structures the N atoms are pyramidalized. The BLYP/3-21G-calculated bond angle C-1,N,C-2 in open *cis-1*-$C_{60}(NCOOH)_2$ is 107.8° (Fig. 9). On the other hand, the corresponding bond angles in closed *cis-1* isomers $C_{60}(NCOOR)_2$ (R = H, Me, Et) is about 65° (BLYP/3-21G, AM1). This shows that a requirement for the planarization of the amide or carbamate N atoms is a comparatively long distance between the bridgehead C atoms, which is best realized by bond opening. This is the only way to ensure a sufficient enlargement of the C,N,C bond angles to about 108°. As expected, for $C_{60}(NH)_2$ or $C_{60}(NR)_2$ (R = alkyl) the N atoms of the imino bridges are pyramidalized for both the open and the closed valence isomers.

Summary and Conclusion

Whether a bisimino[60]fullerene has open or closed transannular [6,6] bonds depends on the addition pattern and the nature of the addend. The following conclusions have been reached:

1) Due to the location of the imino bridges in the same six-membered ring in the *cis-1* adduct, only three [5,6] double bonds have to be introduced upon twofold ring opening. Six of these energetically unfavorable bonds would be required for the hypothetical open structures of the other seven regioisomers (*trans-1* to *cis-2*). In the latter regioisomers the transannular [6,6] bonds are always closed. In addition, only in the case of an open *cis-1* adduct are *all* [5,6] double bonds vinylamines, which are isoelectronic to a resonance-stabilized vinyl anion. This in turn has clearly been established by the chemical shifts of the bridge head C atoms in **1a,b**.
2) In a *cis-1* adduct the closed valence isomer **V** bears a strained planar cyclohexene ring, but the introduction of unfavorable [5,6] double bonds is avoided, whereas in the open valence isomer **VI** no strained planar cyclohexene but formally three [5,6] double bonds are present.
3) In the *cis-1* adducts, open valence isomers **VI** are favored for planar imino bridges like carbamates, and the closed isomers **V** are favored for pyramidalized imino bridges like alkylimines or HN.
4) Carbamates or amides prefer planar arrangements of the nitrogen due to resulting favorable conjugation of the free electron pair with the carbonyl group. This has consequences for imimo[60]fullerenes, since the planar arrangement of the carbamate N atoms and the required enlargement of the bond angles between C-1,N,C-2 or C-3,N,C-4 are most favorably realized if the transannular [6,6] bonds are open.

Hence, the balance of three competitive effects, namely, introduction of unfavorable [5,6] double bonds, strain due to planar cyclohexene rings, and the possibility of favorable nitrogen planarization (for example in carbamates), determine whether the transannular [6,6] bonds are open or closed.

Further investigations on the chemistry of the open valence isomers **1a** and **1b**, such as the cleavage of the activated [5,6] double bonds with $^1O_2$ and their ability to serve as precursors for heterofullerenes[21] "$C_{59}N$", are currently under way.

Experimental Section

^{1}H and ^{13}C NMR: Bruker AC250, JEOL JNM EX 400 and JEOL JNM GX 400; MS: Varian MAT 311 A (EI) and Finnigan TSQ70 (FAB); IR: Bruker IFS48; UV/Vis: Shimadzu UV 3102 PC; HPLC preparative: Shimadzu SIL 10A, SPD 10A, CBM 10A, LC 8A, FRC 10A (Grom-Sil 100 Si, NP1, 5 μ, 25 × 4.6); TLC (Riedel-de Haën, silica gel 60 F 254). Reagents were prepared according to commonly used 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).

1,6-Azahomo[60]fullerene (10c): Trifluoroacetic acid (2 mL) was added to a solution of *N*-(*tert*-butyloxycarbonyl)-1,6-azahomo[60]fullerene (40 mg, 0.048 mmol) in toluene (50 mL). After 16 h almost no starting material could be detected by TLC (SiO_2, toluene/heptane 8:2). The reaction product **10c** was purified by flash chromatography on silica gel using toluene/hexane 8:2 as eluent. After the solvent had been removed, the residue was washed twice with diethyl ether and dried in vacuo (yield: 33.8 mg, 0.046 mmol, 96.8%). ^{13}C NMR (100.5 MHz, CS_2, 31 °C, C_6D_6): δ = 145.37, 144.80, 144.65, 144.59, 144.34, 144.04, 143.92, 143.85, 143.45, 143.20, 143.10, 142.08, 141.89, 140.41, 140.41, 139.74, 139.45, 139.19; IR (KBr): $\tilde{\nu}$ = 3230, 1564, 1458, 1190, 1117, 1082, 1018; 795, 527 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} = 260, 328, 547 nm; MS (FAB, 3-NBA): *m/z* (%): 736 (50) [M^+ + H], 720 (100) [C_{60}^+].

***cis-1*-Bis(alkoxycarbonylimino)tetrahydro[60]fullerenes:**

Method A—with the example of *cis-1*-bis(*tert*-butyloxycarbonylimino)tetrahydro[60]fullerene (**1b**): C_{60} (1 g, 1.388 mmol) was dissolved in 1-chloronaphthalene (35 mL) and heated to 160 °C. *tert*-Butyl azidoformate (1.2 g, 8.383 mmol) in 1-chloronaphthalene (3 mL) was added within five minutes, and the reaction mixture was stirred for 15 min. Chromatography on silica gel with toluene/hexane 7:3 as eluent and evaporation yielded 15.0 mg of product (0.016 mmol, 1.1%). ^{13}C NMR (62.9 MHz, CS_2, 31 °C, $CDCl_3$): δ = 151.43, 146.35 (1 C), 145.81, 145.40, 145.26, 144.48, 144.31 (1 C), 144.18, 143.62, 143.17, 142.99, 142.97 (4C), 142.93, 142.86, 142.76, 142.74, 142.48, 142.42, 140.93, 140.76, 140.58, 140.42 (1 C), 140.31, 139.83, 139.83, 139.48 (1 C), 139.41, 138.96, 137.58, 137.28, 134.74, 128.09, 114.60, 82.16, 27.62; ^{1}H NMR (250 MHz, CS_2, 25 °C, $CDCl_3$): δ = 1.44 (s); IR (KBr): $\tilde{\nu}$ = 2976, 2928, 1736, 1439, 1392, 1368, 1311, 1250, 1155, 527 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 259 (131300), 337 (37100), 555 (1300) nm; MS (FAB, 3-NBA): *m/z* (%): 950 (20) [M^+], 750 (30) [$C_{60}N_2H_2^+$], 722 (100) [$C_{59}N^+$], 720 (80) [C_{60}^+].

Method B—with the example of *cis-1*-bis(ethoxycarbonylimino)tetrahydro[60]fullerene (**1a**): A solution of 1,2-(ethyloxycarbonylimino)-1,2-dihydro[60]fullerene (**9a**) (411 mg, 0.50 mmol) and ethyl azidoformate (100 μL, 117 mg, 0.98 mmol) in 1-chloronaphthalene (20 mL) was stirred for 4 d at 70 °C. After the addition of toluene (200 mL) the reaction mixture was heated under reflux for 30 min. The product **1a** was separated from the starting material and minor amounts of regioisomeric bisadducts on silica gel with toluene as eluent (yield: 41.1 mg, 0.046 mmol, 9.2%). ^{13}C NMR (62.9 MHz, CS_2, 31 °C, $CDCl_3$): δ = 152.62, 146.47 (1 C), 145.93, 145.56, 145.34, 144.53, 144.43 (1 C), 144.27, 143.74, 143.19, 143.11, 143.02, 142.84 (4C), 142.77 (4C), 142.59, 140.97, 140.84, 140.77 (1 C), 140.73, 140.29, 139.96, 139.32, 139.16 (1 C), 138.97, 137.75, 137.18, 134.93, 128.09, 114.73, 62.65, 14.32 (for ^{13}C NMR data of ^{15}N labeled **1a** see ref. [22]); ^{1}H NMR (250 MHz, CS_2, 25 °C, $CDCl_3$): δ = 4.14 (dq, ^3J(H,H) = 7 Hz, 4H; CH_2), 1.28 (t, ^3J(H,H) = 7Hz, 6H; CH_3); IR (KBr): $\tilde{\nu}$ = 2979, 2926, 1730, 1599, 1521, 1441, 1366, 1301, 1285, 1199, 1112, 1037, 765, 524 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 549 (1300), 338 (37600), 260 (133000) nm; MS (FAB, 3-NBA): m/z (%): 894 (50) [M^+], 722 (100) [$C_{59}N^+$], 720 (95) [C_{60}^+].

***cis-1*-Bis(imino)tetrahydro[60]fullerene (1c):** Trifluoroacetic acid (2 mL) was added to a solution of *cis-1*-bis(*tert*-butyloxycarbonylimino)tetrahydro[60]fullerene (**1b**) (15 mg, 0.016 mmol) in toluene (50 mL), and the resulting mixture was stirred until TLC (SiO_2, toluene) showed no starting material (20 h). The solvent was removed and the residue was washed twice with toluene and diethyl ether (Yield: 11.4 mg, 95%). ^{13}C NMR (100.5 MHz, [D$_5$]pyridine, 25 °C): δ = 148.03, 146.93, 146.77, 146.57, 146.33, 145.48, 145.24, 145.22, 144.85, 144.80, 144.58 (1 C), 144.27, 144.25, 144.23, 143.85, 143.77, 143.42, 143.24 (1 C), 143.11, 142.75 (1 C), 142.28, 141.44, 140.75, 140.56, 140.07, 139.97, 137.79 (1 C), 136.86, 91.68, 74.71; IR (KBr): $\tilde{\nu}$ = 3288, 1429, 1170, 528 cm^{-1}. UV/Vis (toluene): λ_{max} (ε) = 424 (4600), 325 (38100) nm; MS (FAB, 3-NBA) m/z (%): 766 (10) [M^+ + O], 720 (100) [C_{60}^+].

Preparation of the regioisomers 1a–7a of bis(ethyloxycarbonylimino)tetrahydro[60]fullerene: Ethyl azidoformate (200 µL, 4.101 mmol) in 1,1,2,2 tetrachloroethane (4 mL) was added within 20 min to a refluxing mixture of C_{60} (2 g, 2.775 mmol) in 1,1,2,2-tetrachloroethane (TCE) (500 mL). The solvent was evaporated, and the residue dissolved in CS_2. To remove C_{60}, monoadducts, and trisadducts the solution was chromatographed twice on silica gel with toluene/hexane 8:2 as eluent. Preparative HPLC (Grom-Sil 100 Si, NP1, 5 µ) of the resulting bisadducts with toluene yielded mixtures of the *trans-1*/*trans-2* and *trans-3*/*trans-4* regioisomers and the pure *e*, *cis-3*, and *cis-1* regioisomers. The mixtures were separated by HPLC using toluene/hexane 8:2. The isolated yields of the bisadducts **1a–7a** are: 30.0 mg (0.033 mmol, 2.4%) for **1a**, 4.5 mg (0.005 mmol, 0.4%) for **2a**, 18.6 mg (0.021 mmol, 1.5%) for **3a**, 17.0 mg (0.019 mmol, 1.4%) for **4a**, 15.2 mg (0.017 mmol, 1.2%) for **5a**, 38.5 mg (0.043 mmol, 3.1%) for **6a**, and 16.9 mg (0.019 mmol, 1.4%) for **7a**.

2a (*trans-1*): ^{1}H NMR (250 MHz, CS_2, 25 °C, $CDCl_3$): δ = 4.79 (q, ^3J(H,H) = 7 Hz, 4H; CH_2), 1.68 (t, ^3J(H,H) = 7 Hz, 6H; CH_3); IR (KBr): $\tilde{\nu}$ = 2922, 2851, 1734, 1656, 1374, 1329, 1144, 988, 527 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} = 258, 317, 451, 480 nm; MS (FAB, 3-NBA): m/z (%): 807 (25) [M^+ − NCOOEt], 720 [C_{60}^+].

3a (*trans-2*): ^{1}H NMR (250 MHz, CS_2, 25 °C, $CDCl_3$): δ = 4.56 (q, ^3J(H,H) = 7 Hz, 4H; CH_2), 1.56 (t, ^3J(H,H) = 7 Hz, 6H; CH_3); ^{13}C NMR (62.9 MHz, CS_2, 25 °C, $CDCl_3$): δ = 155.08, 145.96, 145.72, 145.51, 145.44, 145.40, 144.93 (4C), 144.30, 144.16, 143.91, 143.87, 143.62, 143.23, 143.10, 143.06, 142.82, 142.70, 142.48, 142.36, 141.86, 141.73, 141.65, 141.52 (4C), 141.29, 139.99, 138.54, 138.34, 81.84, 80.99, 63.94, 14.62; IR (KBr): $\tilde{\nu}$ = 2976, 2930, 1745, 1407, 1226, 1095, 1038, 987, 527 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 242 (126100), 256 (123500), 300 (47100) [sh], 316 (42400) [sh], 400 (5100) [sh], 412 (3300) [sh], 424 (3100), 474 (1800), 621 (700), 680 (300) nm; MS (FAB, 3-NBA): m/z (%): 894 (80) [M^+], 720 (100) [C_{60}^+].

4a (*trans-3*): ^{1}H NMR (250 MHz, CS_2, 25 °C, $CDCl_3$): δ = 4.48 (q, ^3J(H,H) = 7 Hz, 4H; CH_2), 1.49 (t, ^3J(H,H) = 7 Hz, 6H; CH_3); ^{13}C NMR (62.9 MHz, CS_2, 25 °C, $CDCl_3$): δ = 154.77, 146.67, 146.31, 145.92, 145.48, 145.42, 145.42, 145.29, 145.02, 144.89, 144.46, 144.40, 144.14 (4C), 144.01, 143.87, 143.50, 143.27, 143.24, 142.80, 142.72, 142.43, 142.35, 142.11, 141.83, 141.35, 140.31, 140.05, 139.19, 81.31, 80.83, 63.83, 14.56; IR (KBr): $\tilde{\nu}$ = 2976, 2930, 1745, 1407, 1230, 1095, 1036, 980, 528 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 246 (105900), 315 (31800) [sh], 408 (2700), 419 (1800), 490 (1900) nm; MS (EI): m/z (%): 894 (10) [M^+], 720 (100) [C_{60}^+].

5a (*trans-4*): ^{1}H NMR (250 MHz, CS_2, 25 °C, $CDCl_3$): δ = 4.47 (q, ^3J(H,H) = 7 Hz, 4H; CH_2), 1.47 (t, ^3J(H,H) = 7 Hz, 6H; CH_3); ^{13}C NMR (62.9 MHz, CS_2, 25 °C, $CDCl_3$): δ = 154.97, 147.61 (1C), 146.62 (1C), 145.98, 145.89, 145.19, 145.03, 144.90, 144.69 (1 C), 144.62, 144.26, 144.11, 144.04, 143.69, 143.18, 143.11, 142.90, 142.59, 142.58, 142.07, 142.00, 141.90, 141.63, 141.41 (3C), 140.95, 140.62, 140.57, 139.93, 139.29, 137.11, 80.42, 79.94, 63.79, 14.54; IR (KBr): $\tilde{\nu}$ = 2975, 2930, 1744, 1410, 1229, 1095, 1036, 980, 528 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} = 249, 314, 469, 677 nm; MS (FAB, 3-NBA): m/z (%): 894 (70) [M$^+$], 720 (100) [C_{60}^+].

6a (*e*): ^{1}H NMR (250 MHz, CS_2, 25 °C, $CDCl_3$): δ = 4.44 (m, 4H; CH_2), 1.45 (t, ^3J(H,H) = 7 Hz, 3H; CH_3) 1.44 (t, ^3J(H,H) = 7 Hz, 3H; CH_3); ^{13}C NMR (62.9 MHz, CS_2, 25 °C, $CDCl_3$): δ = 155.25, 155.13, 146.95, 146.29, 145.70, 145.49 (4C), 145.35 (1 C), 145.06, 144.97, 144.78, 144.40 (4C), 144.28 (1 C), 144.13 (4C), 143.87, 143.81, 143.28, 143.15 (4C), 143.09, 142.65 (6C), 142.09, 141.83, 141.65, 141.56, 140.04, 139.23, 80.92 (1 C, sp^3), 80.40, 79.58 (1 C, sp^3), 64.01, 63.99, 14.54, 14.48; IR (KBr): $\tilde{\nu}$ = 2975, 2930, 1744, 1409, 1231, 1095, 1035, 979, 526 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 250 (121300), 307 (46800), 406 (3000), 417 (2800), 475 (2700) nm; MS (EI): m/z (%): 894 (5) [M^+], 807 (5) [M^+ − NCOOEt], 750 (10) [$C_{60}N_2H_2^+$], 720 (100) [C_{60}^+].

7a (*cis-3*): ^{1}H NMR (250 MHz, CS_2, 25 °C, $CDCl_3$): δ = 4.41 (q, ^3J(H,H) = 7 Hz, 4H; CH_2), 1.44 (t, ^3J(H,H) = 7 Hz, 6H; CH_3); ^{13}C NMR (62.9 MHz, CS_2, 25 °C, $CDCl_3$): δ = 154.38, 145.53, 145.24, 145.08, 144.94, 144.84, 144.44, 144.28, 144.24, 144.19, 144.03, 143.70, 143.69, 143.41, 143.06, 142.97, 142.90 (4C), 142.62, 141.60, 141.46, 141.33, 141.12, 141.02, 140.48, 139.60, 138.59, 137.85, 134.15, 86.66, 84.03, 63.73, 14.47; IR (KBr): $\tilde{\nu}$ = 2975, 2929, 1744, 1439, 1407, 1233, 1095, 1038, 979, 526 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 255 (99900), 319 (31300), 443 (1600), 481 (1600), 683 (200) nm; MS (FAB, 3-NBA): m/z (%): 894 (60) [M^+], 720 (100) [C_{60}^+].

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