Exploiting the Confined Reactivity of C_{2v}-Symmetrical Pentakis-Adducts of [60]Fullerene: Regioselective Formation of Hexakis-, Heptakis-, and Octakis-Adducts with Novel Addition Patterns by Addition of Diazomethane Followed by Dinitrogen Extrusion

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Dedicated to *Edgar Heilbronner* on the occasion of his 80th birthday

A series of hexakis- to octakis-adducts of C_{60} with novel addition patterns was synthesized by 1,3-dipolar cycloaddition of diazomethane (CH_2N_2) to pentakis-adducts, whose reactivity is confined to a single 6-6 bond (bond at the intersect between two hexagons), followed by thermal N_2 extrusion and rearrangement. Starting from pentakis-adducts **1a**,**b** or **13**, hexakis-adducts (±)-**3a**,**b** and (±)-**17** with one 6-5 open methano bridge (bridge at the junction between a hexagon and a pentagon) were obtained in high yield (*Schemes 1* and *6*). Further conversion with CH_2N_2 at -80 to $-60°$ provided heptakis-adducts **6a**,**b** and **18**, respectively, with two 6-5 open methano bridges (*Schemes 2* and *6*). Upon reacting (±)-**3a**,**b** at 0° with a large excess of CH_2N_2, octakis-adducts, (±)-**5a**,**b** with three 6-5 open methano bridges were obtained (*Scheme 2*). Oxidation of the 6-6 double bond, from which the two vicinal methano bridges in heptakis-adducts **6a** and **18** depart, did not give the desired diketones with an opened fullerene shell, but only led to the 1,2-diols **14** and **19**, respectively (*Schemes 5* and *6*). The nature of the addends in the various addition patterns did not affect the regioselectivity of the 1,3-dipolar cycloaddition of CH_2N_2 and the subsequent N_2-extrusion process. The reactivity was, however, affected by the nature of the addends, and compounds bearing only fused cyclopropane rings were found to be better dipolarophiles than those bearing both fused cyclopropane and cyclohexene rings. Frontier-orbital theory provided reliable models for rationalizing both the occurrence and regioselectivity of the observed cycloaddition processes. The regioselectivity of the thermal and photochemical N_2 extrusion from CH_2N_2 adducts of highly functionalized C_{60} derivatives is identical to that observed for CH_2N_2 adducts of the parent fullerenes C_{60} ($C_{61}H_2N_2$) or C_{70} ($C_{71}H_2N_2$). It is also similar to that previously reported by *Klärner et al.* for the thermal and photochemical N_2 elimination from diazoalkane-toluene adducts. The experimental results, together with high-level *ab initio* and density-functional calculations, provide strong evidence that thermal N_2 extrusion from all of these pyrazoline derivatives proceeds *via* a common mechanism, an eight-electron, orbital-symmetry-controlled $[2\pi_s + 2\pi_s + 2\sigma_a + 2\sigma_s]$ concerted process *via* an aromatic transition state (*Schemes 7* and *8*).

1. Introduction. The 1,3-dipolar cycloaddition of diazomethane (CH_2N_2) to C_{60} or C_{70} occurs at 6-6 bonds under formation of isolable pyrazoline derivatives [1][2]. Photolysis of these intermediates under N_2 extrusion provides an isomeric mixture of methanofullerenes, namely 6-6 closed ones, with a cyclopropane ring fused to the bond between two six-membered rings, and 6-5 open ones, in which the methano group bridges the open junction between a six- and a five-membered ring [2], similar to the bonding in 1,6-methano[10]annulene [3]. In contrast, thermolysis of the pyrazolines proceeds with high regioselectivity and yields 6-5 open adducts almost exclusively [1][2].

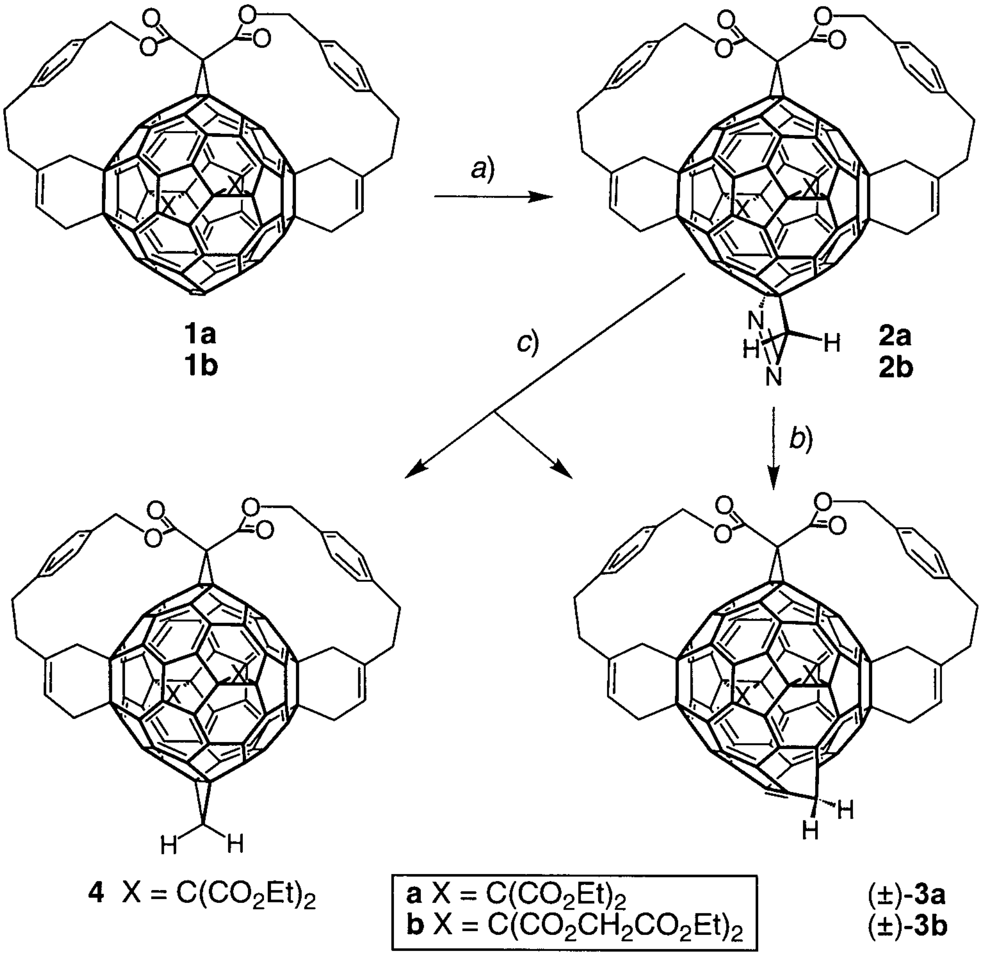
We became interested in exploring whether CH_2N_2 would still add to highly functionalized C-spheres of considerably reduced electrophilicity and dienophilic character [4], and whether the product distribution obtained by N_2 extrusion from the intermediate pyrazolines would be similar to that observed for the parent fullerenes (for a preliminary communication of parts of this work, see [5]). The C_{2v}-symmetrical pentakis-adducts **1a** and **1b** (*Scheme 1*), obtained by tether-directed remote functionalization [6], were chosen as starting materials in this investigation, since their reactivity is confined to a single 6-6 bond in pseudo-octahedral position [7]. This bond is sterically well-accessible and electronically activated by four addends in *e* (equatorial) position (for the naming of addition patterns, see [8]). Here, we report the synthesis and physical properties of a series of hexakis- to octakis-adducts with novel addition patterns by attack of CH_2N_2 at this bond, followed by thermal N_2 extrusion and rearrangement (for the preparation of other types of hexakis-adducts, see the preceding paper [9] and refs. cit. therein).

2. Results and Discussion – 2.1. *Formation of Hexakis-Adducts.* When **1a** or **1b** in $CHCl_3$ was treated with a 35–60-fold excess of etheral CH_2N_2 at 0° (*Scheme 1*), the color of the solution changed within 90 min from orange (typical of the starting pentakis-adduct) to bright-yellow, the characteristic color of hexakis-adducts with a pseudo-octahedral addition pattern. The formed dihydropyrazoles **2a** (71%) and **2b** (93%) were found to be thermally quite unstable and to undergo a rearrangement at 20° within a few days to a new orange-colored product, both in solution and in the solid state. Prolonged storage of **2b** in the solid state at $-20°$ under N_2 led to decomposition to more polar products, probably due to slow oxidation by residual O_2. Thus, the characterization of the dihydropyrazoles had to be carried out immediately after their synthesis.

The identity of the two C_s-symmetrical dihydropyrazoles was confirmed by NMR spectroscopy. The ^1H-NMR spectrum ($CDCl_3$) displayed one *singlet* at *ca.* 5.7 ppm for the enantiotopic CH_2 protons in the dihydropyrazole ring. The ^{13}C-NMR spectra ($CDCl_3$) showed 33 (out of 35 expected) $^{13}C(sp^2)$ resonances for **2a** and 38 (out of 39 expected) $^{13}C(sp^2)$ resonances for **2b**. The N=N stretching vibration was weak but clearly visible in the IR spectrum at *ca.* 1570 cm^{-1}. The instability of the dihydropyrazole moiety was apparent in the FAB mass spectra of the two compounds. Only **2a** gives a weak molecular ion, and the base peak $[M-N_2]^+$ in both spectra arises from loss of N_2.

Heating a solution of **2a** or **2b** in CCl_4 to reflux led, within 15 min, to a color change from bright-yellow to orange. This color is very similar to that of pentakis-adducts **1a**,**b**. TLC Analysis (SiO_2; CH_2Cl_2) indicated essentially an quantitative conversion, and both 6-5 open methanofullerenes (±)-**3a** and (±)-**3b** were isolated in 93% yield. The ^1H- and ^{13}C-NMR spectra indicated that the reaction had indeed proceeded highly regioselectively, yielding only one C_1-symmetrical product consistent with the structures of (±)-**3a** and (±)-**3b**. Thus, the thermal decomposition of the dihydropyrazole in a higher adduct proceeds in analogy to that reported for dihydropyrazole adducts of pristine C_{60} and C_{70}. Loss of N_2 was confirmed by the FAB mass spectra, which showed the molecular ion as the base peak. The C_1 symmetry is apparent in the ^1H-NMR signals arising from the diastereotopic alkene protons in the two cyclohexene rings, which are split into two overlapping *triplets* at *ca.* 6.2 ppm. The protons of the bridging methano group in (±)-**3a** resonate as an *AX* system ($J = 9.9$ Hz) at 4.71 and 2.13 ppm [1][2][10]. The downfield resonating proton sits over the former pentagon

Scheme 1. *Hexakis-Adducts by N_2 Extrusion from Dihydropyrazoles* **2a** *and* **2b**



a) CH_2N_2 (35–60 equiv.), $CHCl_3$, 0°, 1.5 h; 71% (**2a**); 93% (**2b**). *b*) CCl_4, reflux, 15 min; 93% ((±)-**3a**,**b**). *c*) *hν* (Medium-pressure Hg lamp, 250 W), C_6D_6, $c = 9.6$ mM, 5–10°, 8 min; 9–21% (combined yield of (±)-**3a** and **4**).

(that was present in the pentakis-adduct before introducing the 6-5 open CH_2 bridge), whereas the upfield resonating proton resides over the former hexagon. The ^{13}C-NMR spectrum of (±)-**3a** contained signals for all six C=O groups, whereas the spectrum of (±)-**3b** featured eight such signals. In addition to these resonances, 54 ((±)-**3a**) and 55 ((±)-**3b**) other $^{13}C(sp^2)$ resonances were observed, in agreement with the proposed C_1 symmetry. The UV/VIS spectra of (±)-**3a**,**b** are very similar to those of pentakis-adducts **1a**,**b** (*Fig. 1*), in agreement with previous studies that showed that a methano-bridged 6-5 open junction represents only a minor perturbation in a fullerene chromophore [1][11]. The number of conjugated fullerene π-electrons in pentakis-adducts **1a**,**b** and hexakis-adducts (±)-**3a**,**b** is identical.

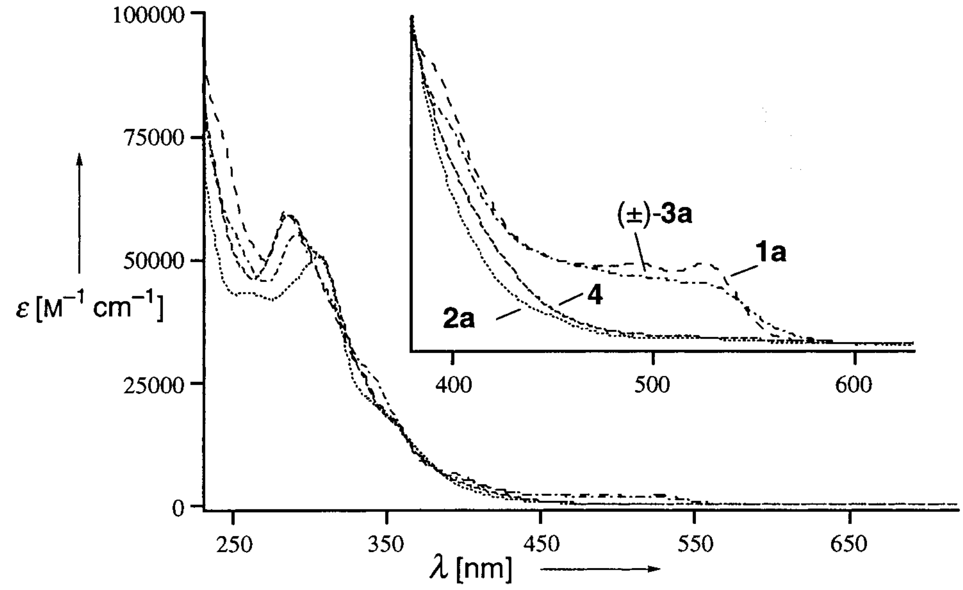


Fig. 1. *UV/VIS Spectra* (CH_2Cl_2) *of pentakis-adduct* **1a** (- - - -), *C_1-symmetrical 6-5 open hexakis-adduct* (±)-**3a** (-·-·- ·), *C_{2v}-symmetrical 6-6 closed hexakis-adduct* **4** (- - - -), *and dihydropyrazole* **2a** (·······)

For investigations of the photochemical N_2 extrusion, dihydropyrazole **2b** could not be used since irradiation in degassed benzene with a medium-pressure Hg lamp (250 W) invariably led to complete, undefined decomposition of the starting material. It became clear that the bis(2-ethoxy-2-oxoethyl) malonate addends were responsible for the particular instability of **2b** under photolytical conditions, since undesirable decomposition was much reduced during irradiation of **2a** under optimized conditions. The yield of isolable product from the photolysis of **2a** was found to be highly concentration-dependent. For example, photolysis of a 0.7 mM or a 23.0 mM solution in C_6D_6 in an NMR tube without cooling led to complete decomposition of the starting material. Best results were obtained at [**2a**] = 9.6 mM while repeatedly cooling the reaction by holding the NMR tube into ice water for *ca.* 15 s, in order to limit the thermal N_2 extrusion. After 8 min, TLC analysis (SiO_2; CH_2Cl_2) indicated that the starting material had completely disappeared, and the C_{2v}-symmetrical hexakis-adduct **4** and the C_1-symmetrical regioisomer (±)-**3a** were obtained in a combined yield between 9–21%. The ratio of the two products was determined by comparison of the ^{1}H-NMR integrals of the resonances corresponding to the enantiotopic protons of the methano bridge in **4** and those corresponding to the diastereotopic methano bridge protons in (±)-**3a**. The isomeric mixture could not be separated by column chromatography. Therefore, **4** was purified by adding CH_2N_2 at 0° to the mixture in CH_2Cl_2, which transformed orange-colored (±)-**3a** into a separable octakis-adduct (see *Sect. 2.2*) while leaving bright-yellow **4** unchanged. The C_{2v}-symmetrical structure of **4** was fully supported by the spectroscopic data. Its UV/VIS spectrum (*Fig. 1*) expectedly resembles closely the one measured for the starting dihydropyrazole **2a**.

The isomer distribution and combined yield of the two regioisomers was found to be strongly dependent on the intervals between the cooling of the reaction during photolysis. Longer periods between coolings increased the formation of the 6-5 open isomer (±)-**3a**, whereas shorter intervals enhanced the relative yield of the 6-6 closed isomer **4** (*Table 1*). These results indicate that at least a part of the 6-5 open isomer (±)-**3a** is formed by thermal N_2 extrusion and not *via* the photolytical pathway. However, more frequent coolings of the reaction decreased the yield of the isolable products, and attempts to increase the relative yield of **4** by photolysis of a frozen, 9.6 mM solution of **2a** in C_6D_6 led to complete decomposition of the starting material.

Table 1. *Dependence of the Product Distribution in the Photolysis of* **2a** *from the Experimental Conditions*

Run[a])	Time intervals between coolings [min][b])	Ratio (±)-**3/4**	Combined yield [%]
I	3.5; 2; 2 × 1	2 : 1	21
II	3.5; 1.5; 3 × 1	1.6 : 1	11
III	3; 5 × 1.2	1 : 1.8	9

[a]) *Runs I–III* were carried out in C_6D_6 in NMR tubes with [**2a**] = 9.6 mM. [b]) Cooling of the samples occurred by holding the NMR tube into ice-water for *ca.* 15 s.

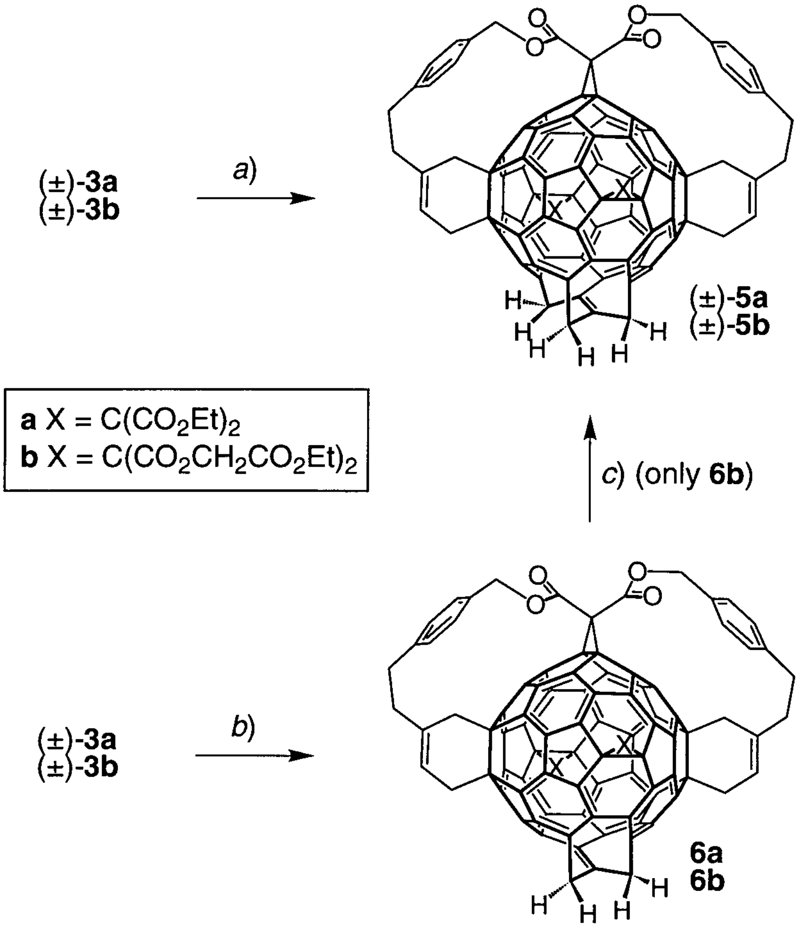
The photolysis of the dihydropyrazole $C_{61}H_2N_2$ formed by addition of CH_2N_2 to C_{60} was also found to be concentration-dependent, producing the 6-6 closed and the 6-5 open isomers in ratios between 2:1 (at low concentration) and 1:4 (at high concentration) [2b][12]. Thus, the photolysis of the highly functionalized fullerene-dihydropyrazole **2a** ultimately gave results similar to those previously reported for C_{60} dihydropyrazole mono-adduct $C_{61}H_2N_2$.

2.2. *Formation of* C_1*-Symmetrical Octakis-Adducts with Three 6-5 Open Methano Bridges.* Treatment of (±)-**3a** or (±)-**3b** with 40–75 equiv. of CH_2N_2 in $CHCl_3$ at 0° led almost immediately to a color change from orange to yellow, indicating that these compounds are more reactive towards CH_2N_2 than the pentakis-adducts **1a**,**b**. After purification by column chromatography and recrystallization, octakis-adducts (±)-**5a** and (±)-**5b** were isolated in 85 and 90% yield, respectively (*Scheme 2*).

The FAB mass spectra of (±)-**5a** and (±)-**5b** showed the molecular ions as the base peaks at *m/z* 1521.2 and 1753.3. The ^{1}H-NMR spectra were consistent with the assigned C_1-symmetrical structures, depicting six *doublets* for the diastereotopic protons of the three CH_2 moieties bridging the 6-5 open junctions. One set of three *doublets* appears downfield between 4.53 and 4.06 ppm, whereas the second set is located upfield between 3.49 and 2.02 ppm. In analogy to the findings for (±)-**3a** (see *Sect. 2.1*) [1][2][10], the protons displaying the downfield-shifted signals are assumed to be located above former pentagons and those with upfield-shifted resonances above former hexagons. The ^{13}C-NMR spectra showed all the C=O resonances expected for C_1-symmetrical compounds, *i.e.*, six for (±)-**5a** and ten for (±)-**5b**. Due to signal overlap, only 53 out of the 66 other $^{13}C(sp^2)$ resonances appeared in the spectrum of (±)-**5a**, whereas the spectrum of (±)-**5b** contained 59 (out of 66) such resonances.

It is not possible to deduce the molecular structures of the C_1-symmetrical octakis-adducts based solely on the spectroscopic data. However, these structures are also

Scheme 2. *Synthesis of Octakis- and Heptakis-Adducts by Addition of CH_2N_2 Followed by N_2 Extrusion*

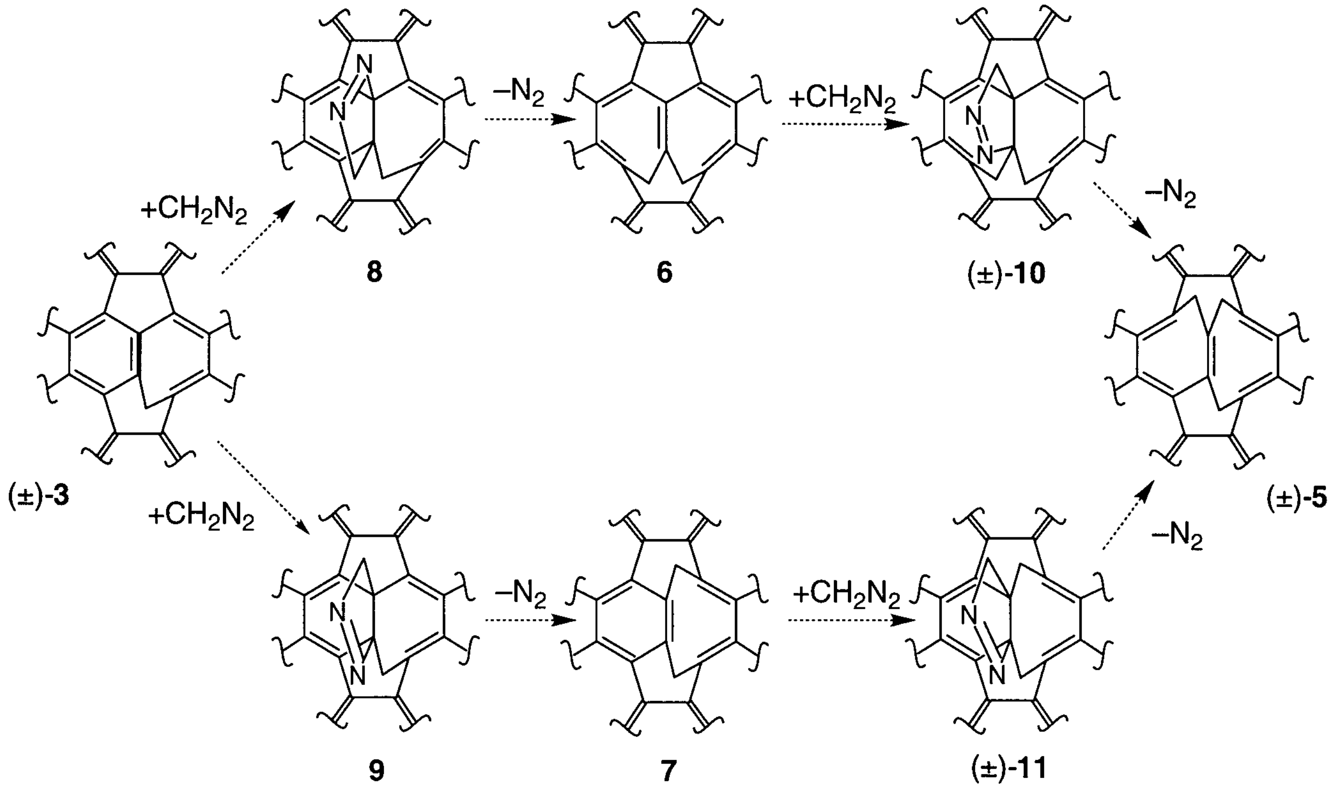


a) CH_2N_2 (40–75 equiv.), $CHCl_3$, 0°, 15 min; 85% ((±)-**5a**; 90% ((±)-**5b**). *b*) CH_2N_2 (20 or 40 equiv.), CH_2Cl_2, −80° → −60°, 10 min; 82% (**6a**); 79% (**6b**). *c*) CH_2N_2 (40 equiv.), CH_2Cl_2, 0°, 15 min; 40% ((±)-**5b**).

strongly supported by chemical-reactivity arguments. The high regioselectivity of the reaction, reflected in the high yield of (±)-**5** (for simplicity, the specifications **a** and **b** are omitted in the following discussion) indicates that the reactivity of each of the precursor molecules (*i.e.*, (±)-**3**, and **6** and/or **7**; *Scheme 3*) must be limited to a single bond. If this were not the case, one would expect the formation of more than one product. Taking this into consideration, the following assumptions were made, based on which the structure of (±)-**5** was proposed:

i) 1,3-Dipolar cycloaddition of CH_2N_2 can only occur at the double bonds in the methano-bridged pyracylene subunit of the fullerene depicted in *Scheme 3*. This may be assumed since all other double bonds are sterically hardly accessible as they are in a *cis-1* relationship [8] to addends already in place.

Scheme 3. *Possible Reaction Pathways Leading to Octakis-Adduct* (±)-**5**. The reactive 'central' double bond in starting material (±)-**3** is highlighted in bold. For clarity, the fullerene is shown only in part and the specifications **a** and **b** are omitted.



ii), The reactivity of hexakis-adduct (±)-**3** is confined to the double bond that is part of the pseudo-octahedral addition pattern (highlighted in bold in *Scheme 3*). This assumption is supported by semi-empirical MO calculations (AM1 (Austin Model 1) [13] and PM3 (Parametric Method 3) [14]), which yield the largest coefficients in the LUMO (lowest unoccupied molecular orbital) at the C-atoms of this double bond.

iii) N_2 Extrusion of the intermediate dihydropyrazoles **8** or **9** proceeds regioselectively to the bis-6-5 open methanofullerenes **6** or **7**, respectively.

iv) The reactivity of the heptakis-adducts **6** and **7** is limited to the double bond from which the two methano bridges depart and which is part of the pseudo-octahedral addition pattern.

If these assumptions proved to be true, then the reaction sequence to the octakis-adduct (±)-**5** can proceed *via* the dihydropyrazoles **8** and/or **9**, and the bis-6-5 open bridged derivatives **6** and/or **7**. Once the dihydropyrazoles (±)-**10** or (±)-**11** are formed, the final N_2 extrusion must process regioselectively to the tris-6-5 open bridged octakis-adduct (±)-**5**. If the CH_2 moiety bridged the 'central' 6-6 bond (central with respect to the pyracylene shown in *Scheme 3*) of heptakis-adducts **6** or **7**, the respective products would be C_s-symmetrical, which is incompatible with the spectral data.

Note that addition of CH_2N_2 to **6** could lead to a regioisomer of (±)-**10** (not shown) in which the C-atom of CH_2N_2 is attached to the C-atom carrying the geminal CH_2 moieties. However, upon N_2 extrusion, the newly introduced methano group would have to bridge the 'central' 6-6 bond from which the two other CH_2 groups depart, leading to a C_s-symmetrical compound, which can be ruled out based on the spectroscopic data of (±)-**5**. Also, N_2 extrusion from **9** could, in principle, lead to a C_2-symmetrical product in which the two vicinal methano bridges adopt a *trans*-orientation with respect to the 'central' double bond, as compared to the *cis*-orientation depicted for **7**. However, both AM1 and PM3 calculations show this isomer to be 15–20 kal mol^{-1} less stable than **6** or **7**, and it can probably be dismissed as a potential intermediate. The large difference in stability is the result of extensive skewing of the 'central' double bond (over 20°) if the vicinal CH_2 bridges are in the *trans*-configuration. This large difference in stability between *cis*- and *trans*-isomers would be, at least partially, reflected in the transition state for N_2 extrusion from **9**, thereby strongly disfavoring formation of the *trans*-product.

2.3. *Regioselective Synthesis of Heptakis-Adducts with Two 6-5 Open Methano Bridges.* To prove assumptions *i–iii* made in *Sect. 2.2*, it was necessary to synthesize the intermediate heptakis-adducts **6** and/or **7**. Therefore, it was decided to react hexakis-adducts (±)-**3a**,**b** with an excess of CH_2N_2 at low temperatures. It was assumed that, at low temperatures, the intermediate dihydropyrazoles **8a**,**b** and/or **9a**,**b** (*Scheme 3*) would be stable and would prevent further addition of CH_2N_2 by blocking the reactive 'central' double bond. Subsequent quenching of excess CH_2N_2 and warming the mixture to room temperature would allow the isolation of the resulting heptakis-adduct(s) after N_2 extrusion from the intermediate dihydropyrazoles.

CH_2N_2 (20- or 40-fold excess) was added to (±)-**3a** or (±)-**3b** in CH_2Cl_2 at −80° (*Scheme 2*). The mixture was allowed to warm within 10 min to −60°. At that point, the color of the solution had changed from pale-orange to yellow, indicating that the cycloaddition of CH_2N_2 had taken place, and the excess reagent was immediately quenched with AcOH. Indeed, the reaction proceeded highly regioselectively, producing only the heptakis-adducts **6a** and **6b** in 83 and 79% yield, respectively. The selective formation of **6a**,**b** proved that the 1,3-dipolar cycloaddition of diazomethane occurs only at the 'central' double bond of the pyracylene subunit depicted in *Scheme 3* (assumptions *i* and *ii*), and that N_2 extrusion proceeds regioselectively to form a bis-6-5 open derivative (assumption *iii*). In fact, the result implies that the 1,3-dipolar cycloaddition of CH_2N_2 proceeds highly regioselectively, forming as the only intermediate dihydropyrazole **8** (*Scheme 3*). The regioselectivity of this reaction can be understood upon inspection of the frontier-orbitals of CH_2N_2 and hexakis-adduct (±)-**3**, as calculated on the semi-empirical level (AM1). According to frontier orbital theory, the dipole and the dipolarophile will react in such a way that the atoms with the large orbital coefficients in the HOMO (dipole) and the LUMO (dipolarophile), respectively, and those with small orbital coefficients in the HOMO (dipole) and LUMO (dipolarophile), respectively, will combine (HOMO = highest occupied molecular orbital, LUMO = lowest unoccupied molecular orbital). The calculation of the HOMO of CH_2N_2 yields the largest coefficient (0.580) at the C-atom, followed by the terminal N-atom (0.396). The largest coefficients of the LUMO of (±)-**3** are found at the 'central' double bond, namely at the bridgehead C-atom (0.121) and at the adjacent C-atom of that bond (0.084). The observed regioselectivity leading to **6** exclusively is, therefore, in agreement with frontier orbital theory considerations.

The C_s-symmetry of **6a**,**b** allows the unambiguous structural assignment based on spectroscopic data. The ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) shows two *doublets* at 4.44 and 2.76 ppm (**6a**), and 4.48 and 2.75 ppm (**6b**) for the two enantiotopic protons of the methano bridges. The alkene protons of the cyclohexene moieties appear as one *triplet*. Note that in the other C_s-symmetrical heptakis-adduct **7** (*Scheme 3*), the cyclohexene alkene protons would be diastereotopic, and, therefore, one would expect to observe two *triplets*, similar to the spectrum of (±)-**3a**,**b** (*vide supra*). In the ^{13}C-NMR spectra, the diastereotopic C=O C-atoms of the two simple malonate addends that lie in the plane of symmetry give rise to four (**6a**) and eight (**6b**) resonances of single intensity, whereas the two enantiotopic C=O C-atoms of the anchor malonate residue produce one peak of double intensity, which is compatible only with the proposed geminal relationship of the two methano bridges in **6a**,**b**. In addition to the C=O resonances, the spectrum featured 30 (**6a**) and 32 (**6b**) additional $^{13}C(sp^2)$ resonances, out of the 32 expected for C_s symmetry. In the UV/VIS spectra (CH_2Cl_2), heptakis-adducts **6a**,**b** and octakis-adducts (±)-**5a**,**b** feature similar optical end-absorptions around 530 nm. The absence of a hypsochromic shift upon adding one more methano group bridging a 6-5 open junction underlines once more that this type of bridging represents only a very minor perturbation of the overall π-electron chromophore in the fullerene sphere.

2.4. *The 'Geminal' Heptakis-Adduct* **6b** *is Not an Intermediate in the Formation of Octakis-Adduct* (±)-**5b** *Starting from* (±)-**3b**. To prove assumption *iv* (see *Sect. 2.2*), we reacted heptakis-adduct **6b** with CH_2N_2 (40 equiv.) at 0°, expecting a near quantitative yield of octakis-adduct (±)-**5b** (the yield in the reaction at 0° starting from (±)-**3b** was 90%, *vide supra*). Surprisingly, however, treatment of **6b** with CH_2N_2 at 0° produced octakis-adduct (±)-**5b** in only *ca.* 40% yield in a mixture with at least one other C_1-symmetrical adduct (^{1}H-NMR) (*Scheme 2*). The reduced yield of (±)-**5b** suggests that heptakis-adduct **6b** cannot be the intermediate in the direct formation of (±)-**5b** from

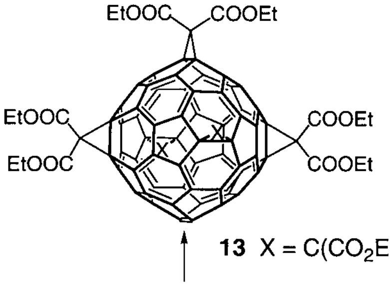
(±)-**3b**. As it is plausible to assume that the double bond in (±)-**3b** in the pseudo-octahedral position remains the most reactive one, the reaction at 0° probably proceeds *via* the vicinally bis-methano-bridged heptakis-adduct **7b** (*Scheme 3*).

According to AM1 calculations, the coefficients in the LUMO of **7** are by far the largest at the C-atoms of the 'central' double bond from which the two vicinal methano bridges depart. Therefore, the 1,3-dipolar addition of CH_2N_2 should produce dihydropyrazole **11** from which, upon N_2 extrusion, the only C_1-symmetrical octakis-adduct that can be formed is (±)-**5**. Note, that the LUMO in heptakis-adduct **6** features only very small coefficients at the C-atoms of the 'central' geminally bis-methano-substituted double bond but larger coefficients at the C-atoms of other double bonds in the bridged pyracylene unit shown in *Scheme 3*. This is in agreement with the observed low regioselectivity of the reaction of **6b** with CH_2N_2 at 0°.

2.5. *Attempted Synthesis of a* C_{2v}*-Symmetrical Nonakis-Adduct with Four 6-5 Open Methano Bridges.* A particularly attractive target molecule is the C_{2v}-symmetrical nonakis-adduct **12**, which would be formally obtained by inserting a methano bridge into the remaining 6-5 bond connecting to the 6-6 bond of octakis-adduct (±)-**5b**, from which the three other CH_2 bridges already depart (*Scheme 4*). However, even prolonged treatment (24 h) of (±)-**5b** with a large excess (≥60 equiv.) of CH_2N_2 at 0° or at 20° did not lead to a reaction and only unchanged starting material was recovered.

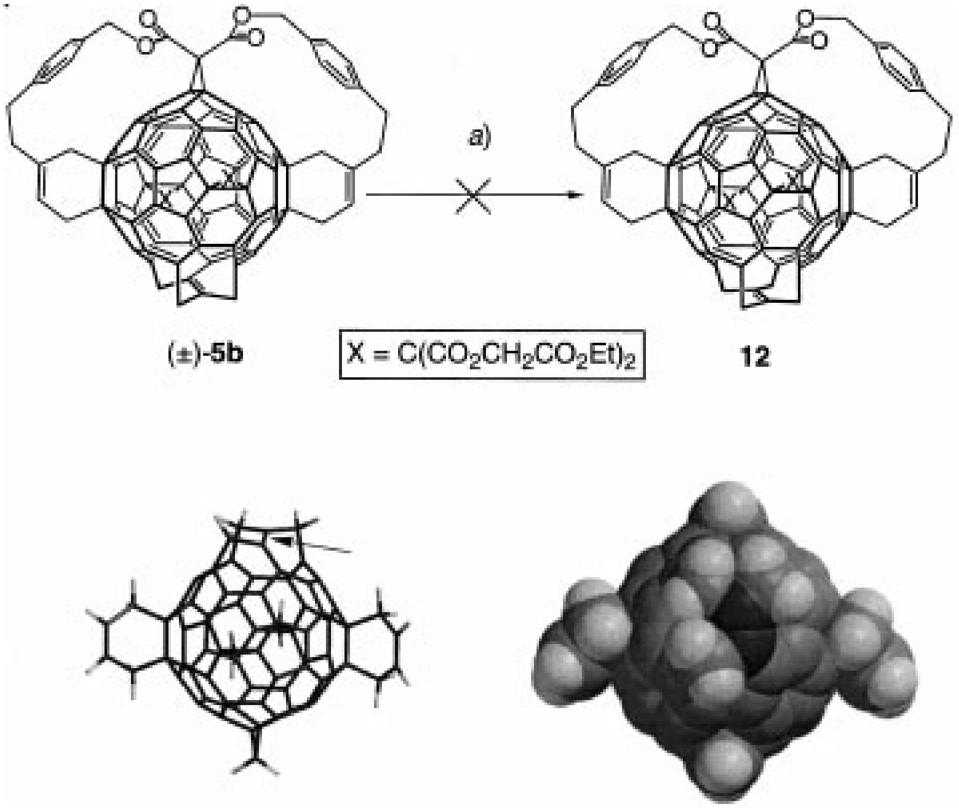
PM3 Calculations on a model for (±)-**5b** (*Scheme 4*), with all substituents on the fused cyclohexenyl and cyclopropyl rings replaced by H-atoms, show that the 6-6 bond, from which the three methano bridges depart, is partially lifted out of the fullerene sphere. Nevertheless, this bond encounters severe steric shielding by the three surrounding CH_2 groups, as revealed by a space-filling model (*Scheme 4*), and this steric crowding most certainly leads to its inertness towards 1,3-dipolar cycloaddition of CH_2N_2.

2.6. *Attempted Oxidative Opening of the Fullerene Sphere in the Higher Adducts.* The opening of the shell of buckminsterfullerene with the objectives of *i*) inserting atoms, ions, or molecules, *ii*) changing the shell and producing novel carbon allotropes upon reclosure, and *iii*) inserting heteroatoms into the shell is an important area of research in contemporary fullerene chemistry [15–17]. We intended to accomplish shell-opening by oxidative cleavage of the reactive 6-6 double bond with the two vicinal CH_2 substituents in heptakis-adduct **6a**, following a strategy previously used by *Hirsch* and co-workers [7]. Oxidation of the analogous 6-6 bond in the pseudo-octahedral addition pattern of pentakis-adduct **13** with $KMnO_4$ gave the vicinal diol, which could



13 X = $C(CO_2Et)_2$

Scheme 4. *Attempted Synthesis of* C_{2v}-*Symmetrical Nonakis-Adduct* (±)-**12**. Shown are also two views of a calculated structure (PM3) of a model for starting material (±)-**5b**, in which, for ease of computing, substituents on the fused cyclohexenyl and cyclopropyl rings have been replaced by H-atoms. The stick model (*left*) shows that the 6-6 bond connected to the three methano bridges (marked by an arrow) is partially lifted out of the fullerene sphere. The space-filling representation (*right*) illustrates the steric shielding of this bond (highlighted in dark grey) by the three methano substituents.



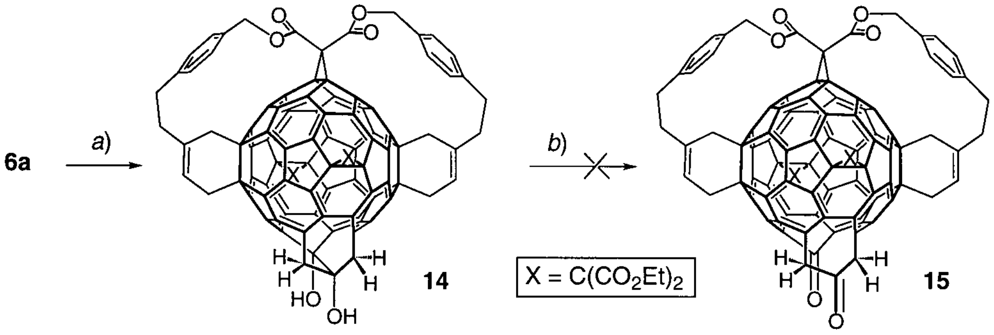
a) CH_2N_2 (60 equiv.), $CHCl_3$, 0° or 20°, 24 h.

not be transformed with $Pb(OAc)_4$ into the corresponding diketone under formation of an open ten-membered ring in the fullerene shell; only the 1,2-dioxetane with an intact fullerene cage was isolated. The authors argued that the rigidity of the fullerene cage was forcing the two C=O groups to align in an almost parallel, eclipsed fashion within *van der Waals* contact, making the ring-opened product very unfavorable.

In heptakis-adduct **6a**, the reactive double bond is partially lifted out of the fullerene sphere by the two vicinal CH_2 bridges. We hoped that this specific geometry would provide extra space and structural flexibility to allow formation of the desired ring-opened dione. An obvious side reaction in the oxidation of this 6-6 bond in **6a** could be the oxidation of the double bonds in the two tethered cyclohexene moieties. However, AM1 calculations produced large coefficients in the HOMO-1 at the C-atoms of the reactive fullerene double bond and no coefficients (neither in the HOMO nor in the HOMO-1) at the C-atoms of the cyclohexene double bonds. We, therefore, expected high regioselectivity in the oxidation reaction.

When **6a** in CH_2Cl_2 was treated with an aqueous solution of $KMnO_4$ (1.1 equiv.) in the presence of [18]crown-6, diol **14** was obtained as a bright-yellow solid in 66% yield after workup and chromatographic purification (*Scheme 5*). No products arising from oxidation of the double bonds in the tethered cyclohexene rings could be detected, in agreement with the computational prediction.

Scheme 5. *Attempted Synthesis of the Shell-Opened Diketone* **15**



a) $KMnO_4$ (1.1 equiv), [18]crown-6, H_2O/CH_2Cl_2, 20°, 2 h, then AcOH, 20°, 2 h; 66%. *b*) $Pb(OAc)_4$ (1.1 equiv.), CH_2Cl_2, 20°, 75 min.

The spectroscopic data of **14** are in agreement with the proposed C_s-symmetrical structure. The ^1H-NMR spectrum shows two *doublets* at 3.84 and 3.62 ppm for the two pairs of enantiotopic protons of the CH_2 bridges. The alkene protons in the cyclohexene moieties appear as one *triplet* at 6.01 ppm, in agreement with the C_s symmetry. One OH group gives a sharp resonance at 4.66 ppm, whereas the signal of the second OH group is obscured by the CH_2 resonances of the diethyl malonate addends between 4.15 and 4.40 ppm; these assignments were further corroborated by H/D exchange upon addition of D_2O to the $CDCl_3$ solution. The C_s symmetry was also supported by the ^{13}C-NMR spectrum that depicted all expected 24 fullerene $^{13}C(sp^2)$ resonances. The FAB mass spectrum contained the molecular ion as the base peak at *m/z* 1541.6, the next most prominent signal at *m/z* 1523.1 (45% relative intensity) arising from loss of H_2O. The IR spectrum (CCl_4) depicted a sharp band at 3734 cm^{-1} and a broad one at 3396 cm^{-1} for the stretches of free and H-bonded OH, respectively.

Addition of $Pb(OAc)_4$ to a solution of **14** in CH_2Cl_2 led to complete disappearance of starting material within 75 min (TLC). Workup and chromatography (SiO_2; CH_2Cl_2/AcOEt 9:1) provided a yellow-green solid in 62% yield. Although the FAB mass spectrum showed a weak peak (18% relative intensity) for the expected molecular ion of **15** at *m/z* 1539.1, the formation of the C_s-symmetrical dione or of the corresponding 1,2-dioxetane (similar to the one obtained by *Hirsch* and co-workers [7]) could not be confirmed by other spectroscopic methods (^1H- and ^{13}C-NMR, and IR). At present, the constituency of the isolated solid, which according to chromatographic analysis is a single compound, remains unknown.

2.7. *Higher Adducts by Addition of CH_2N_2 to an All-cyclopropanated* C_{2v}*-Symmetrical Pentakis-Adduct Followed by* N_2 *Extrusion*. In a previous investigation [4a], we had shown that a C_{60} tris-adduct with three fused cyclopropane rings featured significantly different properties than a tris-adduct with the same addition pattern but with one fused cyclopropane and two fused cyclohexene rings. Thus, the all-cyclopropanated derivative exhibited a lower-energy optical gap, more reversible one-electron reductions at more anodic potentials, a lower LUMO energy, and a higher electrophilic reactivity. We were interested in exploring whether similar differences would exist between pentakis-adducts **1a**,**b**, with two fused cyclohexene and three cyclopropane rings, and the all-cyclopropanated analog **13** in their reactivity against CH_2N_2. For this study, we prepared **13** by the template-mediated route *via* reversible formation of a fullerotriazoline, introduced by *Hirsch* and co-workers [7].

Addition of etheral CH_2N_2 (20-fold excess) to a solution of **13** in $CHCl_3$ at 0° and stirring at this temperature for 20 min provided dihydropyrazole **16** as a bright-yellow solid in 94% yield (*Scheme 6*). The shorter reaction time necessary for the synthesis of **16** as compared to the preparation of **1a**,**b** (60 min) indicated that the all-cyclopropanated pentakis-adduct **16** is a better dipolarophile than **1a**,**b**. The C_s-symmetrical structure of **16** was supported by the ^{1}H-NMR spectrum (200 MHz, $CDCl_3$), which showed a single resonance at 5.95 for the enantiotopic CH_2 protons in the dihydropyrazole ring, and the ^{13}C-NMR spectrum (50 MHz, $CDCl_3$), which featured the 24 resonances expected for fullerene $^{13}C(sp^2)$-atoms.

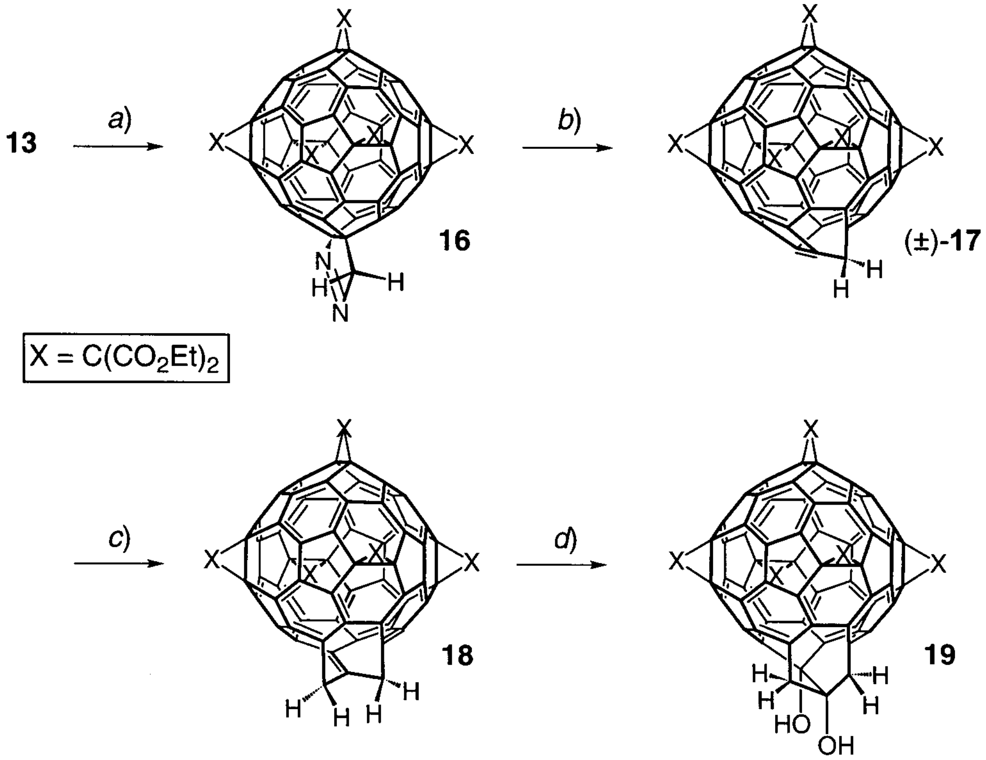
We quantified the difference in chemical reactivity between **1a** and **13** in kinetic runs, in which a freshly prepared etheral solution of CH_2N_2 (0.5 ml, *ca.* 0.76M, *ca.* 100 equiv.) was added to a vigorously stirred solution of pentakis-adduct (0.00338 mmol) in $CHCl_3$ (10 ml) at 0°. The course of the reaction was monitored by taking samples at regular intervals and analyzing the ratio of fullerene starting material and product in each run by HPLC. The conversion of **1a** to **2a** was completed in 96 min ($t_{\mathrm{end}(\mathbf{1a})}$) and the one of **13** to **16** after 22 min ($t_{\mathrm{end}(\mathbf{13})}$). In the presence of the very large excess of CH_2N_2, using the *Eyring* equation, the difference in free enthalpy between the two transition states can be approximated by *Eqn. 1* [18]:

$$\mathrm{R}T\ln[k_{\mathbf{1a}}/k_{\mathbf{13}}] = \mathrm{R}T\ln[t_{\mathrm{end}(\mathbf{13})}/t_{\mathrm{end}(\mathbf{1a})}] = \Delta G^{\ddagger}_{\mathbf{13}} - \Delta G^{\ddagger}_{\mathbf{1a}-} \tag{1}$$

In *Eqn. 1*, $k_{\mathbf{1a}}$ and $k_{\mathbf{13}}$ are first-order rate constants ([s^{-1}]) for the two cycloadditions, $t_{\mathrm{end}(\mathbf{1a})}$ and $t_{\mathrm{end}(\mathbf{13})}$ are the times ([min]) determined for complete consumption of the starting material, and $\Delta G^{\ddagger}_{\mathbf{1a}}$ and $\Delta G^{\ddagger}_{\mathbf{13}}$ ([kcal mol^{-1}]) are the activation-free enthalpies of the two cycloaddition reactions. From this equation, the difference in free enthalpy between the two transition states $\Delta G^{\ddagger}_{\mathbf{13}-} - \Delta G^{\ddagger}_{\mathbf{1a}}$ could be determined as -0.8 kcal mol^{-1}.

This difference in activation free enthalpy must be the result of the different nature of the addends in the two pentakis-adducts. Inspection of PM3-optimized models of **1a** and **13**, in which the substituents on the fused cyclopropane and cyclohexene rings are replaced by H-atoms for ease of computing, indicated that the difference in reactivity does not arise from different pyramidalization of the C-atoms in the reacting 6-6 bond. The calculated pyramidalization *S* (expressed as the difference between 360° and the sum of the three bond angles at the atom) [19] of the two sp^2-C-atoms in this bond

Scheme 6. *Higher Adducts of C_{60} by 1,3-Dipolar Cycloaddition of CH_2N_2, Followed by N_2 Extrusion, Starting from All-Cyclopropanated Pentakis-Adduct* **13**



a) CH_2N_2 (20 equiv.), $CHCl_3$, 0°, 20 min; 94%. *b*) $CHCl_3$, reflux, 5 h; 82%. *c*) CH_2N_2 (25 equiv.), CH_2Cl_2, $-80° \rightarrow -60°$, 10 min; 98%. *d*) $KMnO_4$ (1.1 equiv.), [18]crown-6, H_2O/CH_2Cl_2, 20°, 2 h, then AcOH, 20°, 2 h; 85%.

amounts to 12.0° (in the model for **1a**) and 12.1° (in the model for **13**). Rather, the difference in reactivity originates from differences in the LUMO energy of the pentakis-adducts [4a]. In agreement with the better dipolarophile character of **13**, the energy of its LUMO is calculated to be lower than that of **1a** by 0.14 eV (3.2 kcal mol^{-1}, PM3) and 0.17 eV (3.9 kcal mol^{-1}, AM1), respectively. Again, calculations were performed on the model systems with all substituents on the fused cyclopropane and cyclohexene rings being H-atoms.

Although the nature of the addends affects the reactivity, it does not have an influence on the regiochemistry of further chemical transformations as shown in the following. Similar to the thermal N_2 extrusion from **2a**,**b**, thermal treatment of **16** proceeded with high regioselectivity and yielded exclusively the C_1-symmetrical 6-5 open methanofullerene (±)-**17** in 82% yield as a deep-orange solid. The C_1 symmetry of (±)-**17** is apparent both in the ^1H-NMR spectrum (400 MHz, $CDCl_3$), in which the two diagnostic *doublets* of the diastereotopic methano bridge protons appear at 5.24 and 2.45 ppm, as well as in the ^{13}C-NMR spectrum (100 MHz, $CDCl_3$), which displayed 40 out of the 50 fullerene $^{13}C(sp^2)$-atom as well as nine out of the ten bridgehead $^{13}C(sp^3)$-atom resonances.

Addition of CH_2N_2 (25 equiv.) to (±)-**17** in CH_2Cl_2 at $-80°$, warming within 10 min to $-60°$, and subsequent quenching with AcOH produced the bright-yellow heptakis-adduct **18** in nearly quantitative yield (98%). The addition pattern formed was identical to the one in **6a**,**b** (*Scheme 2*). The C_s symmetry as well as the geminal relationship of the two methano bridges at the 6-5 open junctions were readily deduced from the spectral data. In the ^1H-NMR spectrum (500 MHz, $CDCl_3$), the two pairs of enantiotopic protons in these methano bridges give rise to two *doublets* at 4.80 and 3.02 ppm, respectively. The geminal relationship of the methano groups is apparent from the relative intensity and the number of signals in the ^{13}C-NMR spectrum (125 MHz, $CDCl_3$). The ten C=O C-atoms are grouped into two sets of signals, namely three signals of double intensity arising from the six enantiotopic C=O C-atoms and four signals of single intensity corresponding to the diastereotopic C=O C-atoms, which lie in the plane of symmetry. For the corresponding heptakis-adduct in which the two CH_2 bridges are in a vicinal relation (addition pattern of **7** in *Scheme 3*), one would expect a total of six C=O signals, four of double and two of single intensity. Further confirmation of the molecular structure of **18** comes from the inspection of the fullerene and olefinic $^{13}C(sp^2)$-atom region in the ^{13}C-NMR spectrum that shows all 26 expected signals, 24 of double and two of single intensity (143.07 and 135.88 ppm); the latter ones arising from the diastereotopic C-atoms of the double bond from which the geminal CH_2 groups depart. Again, this observation is only compatible with the proposed structure of **18** as a vicinal relationship of the two CH_2 groups would give rise to 25 signals, all of double intensity.

Fig. 2 shows the UV/VIS spectra (CH_2Cl_2) of the C_1-symmetrical hexakis-adducts (±)-**3a** and (±)-**17** in comparison to those of the C_s-symmetrical heptakis-adducts **6b** and **18**. The insertion of the second 6-5 open methano bridge has a large influence on the position of the optical end-absorption, causing a hypsochromic shift of *ca.* 50 nm. Also visible is the bathochromic shift of the optical end-absorption upon passing from derivatives with three fused cyclopropane and two fused cyclohexene rings to those possessing five fused cyclopropane rings (*i.e.* (±)-**3a** *vs.* (±)-**17**, and **6b** *vs.* **18** [4a]).

In analogy to the synthesis of diol **14** (*Scheme 5*), heptakis-adduct **18** was oxidized with $KMnO_4$ to give the C_s-symmetrical diol **19** (85% yield, *Scheme 6*). The ^1H-NMR spectrum (200 MHz, $CDCl_3$) displayed one broad signal for two OH protons at 4.89 ppm. One *doublet* for the methano bridge protons is obscured by the signals of the CH_2 groups of the malonate ester residues, whereas the other one appears at 3.91 ppm. The IR spectrum of **19** ($CHCl_3$) featured two bands, one sharp one at 3606 cm^{-1} and a broad one at 3465 cm^{-1}, corresponding to the stretches of free and associated OH groups. Similar to the results obtained with **14**, oxidation of diol **19** to produce shell-opened dione was unsuccessful. Thus, treatment of **19** with $Pb(OAc)_4$ (1.1 equiv.) in CH_2Cl_2 led to complete consumption of the starting material within 75 min and to the formation of two new products at higher R_f values (0.67 and *ca.* 0.9 on TLC (SiO_2; CH_2Cl_2/AcOEt 98:2)). Again, the FAB mass spectrum of the crude product contained a peak for the expected molecular ion of the diketone at *m/z* 1571.3. However, as in the attempted preparation of **15** from **14** (*Scheme 5*), the ^1H-NMR spectra of the two

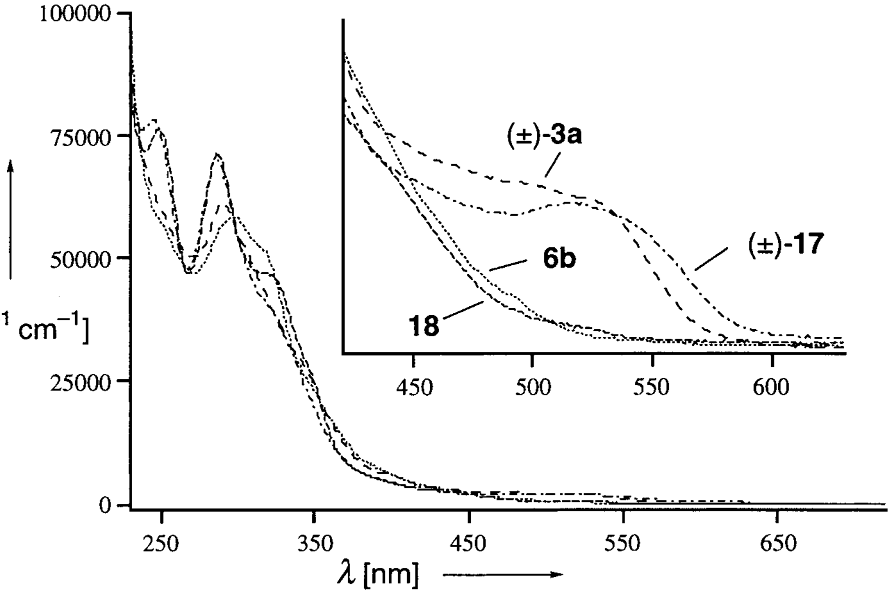


Fig. 2. *UV/VIS Spectra* (CH_2Cl_2) *of the two* C_1*-symmetrical hexakis-adducts* (±)-**3a** (- - - -) *and* (±)-**17** (-·-·-·-), *and the two* C_s*-symmetrical heptakis-adducts* **6b** (·······) *and* **18** (- - - -)

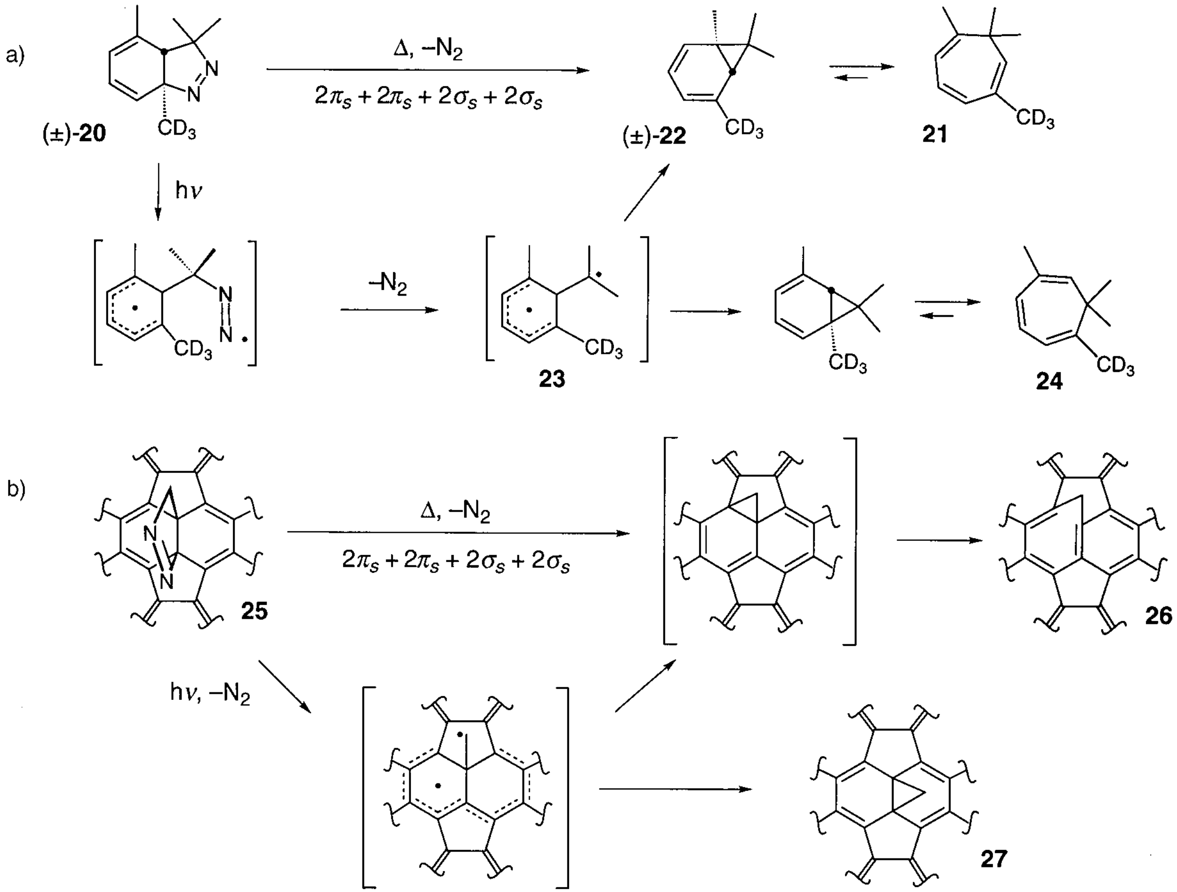
products separated by chromatography showed only very broad, unresolved peaks, and their ^{13}C-NMR spectra also did not display interpretable signals.

2.8. *Origin of the Regioselectivity of the Thermal* N_2 *Extrusion from Fullerodihydropyrazoles.* In the preliminary communication to this work [5], the close similarity of the thermal and photochemical N_2 elimination from CH_2N_2-fullerene adducts to the N_2 elimination from CH_2N_2-toluene adducts [20], which had been previously reported by *Klärner et al.*, was recognized. Starting from (±)-**20**, thermolysis provides with high regioselectivity cycloheptatriene **21**, resulting from ring-opening of the intermediate norcaradiene (±)-**22** (*Scheme 7*). To account for this high regioselectivity, the authors proposed an eight-electron, orbital-symmetry-controlled $[2\pi_s + 2\pi_s + 2\sigma_a + 2\sigma_s]$-concerted mechanism [20a]. Photolysis, in contrast, was proposed to proceed *via* the diradical intermediate **23**, which, upon radical recombination, leads to the observed mixture of regioisomeric cycloheptatrienes **21** and **24**.

Similarly, thermolysis of the fullerene-dihydropyrazole derivatives **25** leads almost exclusively to the formation of 6-5 open methanofullerenes **26**, whereas photolysis produces mixtures of the 6-5 open (**26**) and the 6-6 closed regioisomer **27** (*Scheme 7*).

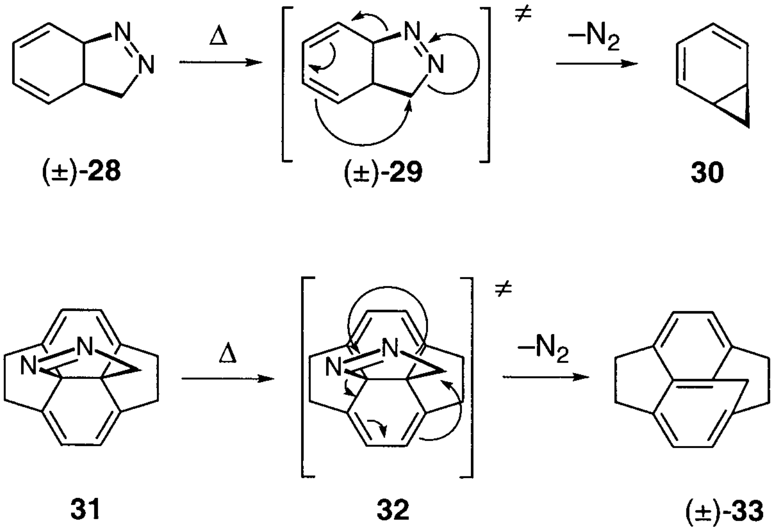
The mechanism for thermal N_2 extrusion was subsequently investigated for model system (±)-**28** (*Scheme 8*) by high-level *ab initio* and density-functional calculations [21]. These calculations showed that N_2 extrusion proceeds *via* the aromatic transition state (±)-**29** to give **30**, thereby fully supporting the proposed eight-electron, $[2\pi_s + 2\pi_s + 2\sigma_a + 2\sigma_s]$ *Woodward-Hoffmann*-allowed mechanism. Further calculations revealed that these results are transferable to N_2 extrusion from more rigid model systems and that N_2 extrusion from **31** proceeds *via* transition state **32** to provide (±)-**33**

Scheme 7. *Proposed Mechanism for the Thermal and Photochemical* N_2 *Extrusion* a) *from Diazopropane Adducts of* m-*Xylene and* b) *from* CH_2N_2 *Adducts from Fullerenes* (shown only in part for clarity)



(*Scheme 8*). In view of the structural analogy of **31** to fullerodihydropyrazoles, it was concluded that the same mechanism is also responsible for the high regioselectivity of the thermal N_2 extrusion from dihydropyrazole-fused C-spheres to give 6-5 open methanofullerenes.

Scheme 8. *Depiction of the Reaction Pathways Found for the Thermal N_2 Extraction from CH_2N_2 Adducts by* Ab Initio *and Density-Functional Calculations*



Here, we provide additional experimental evidence for the validity of this conclusion. We show that the experimentally measured activation energies for the thermal N_2 extrusion from toluene-diazopropane adduct (±)-**34** to give **35** and from fulleropyrazoline **2a** to give (±)-**3a** (*Scheme 9*) are similar.

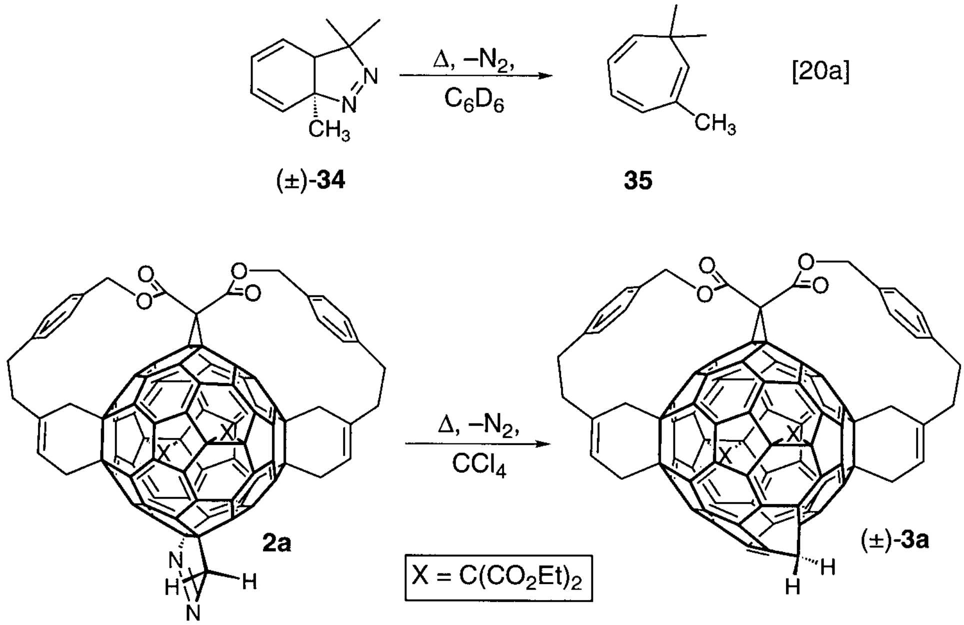
Thermolysis of pyrazoline **2a** was carried out at 313, 323, 333, 340, and 348 K, and both the decrease in starting material as well as the increase in product (±)-**3a** were monitored by HPLC. The conversion proceeds with first-order kinetics, and rate constants were measured as shown in *Table 2*. The activation energy was subsequently determined from an *Arrhenius* plot (*Fig. 3*), yielding $E_a = 27.7 \pm 1.6$ kcal mol^{-1}. For the first-order conversion from (±)-**34** to **35**, *Klärner et al.* had previously determined an activation energy of $E_a = 25.09 \pm 0.13$ kcal mol^{-1} [20a].

We take the identical regioselectivity and the similar activation energy as strong experimental evidence that the same mechanism – as shown in *Scheme 8* – is operative in the thermal N_2 extrusion from **2a** to give (±)-**3a** and in the conversion of (±)-**34** to **35** (*Scheme 9*). It can be assumed that this mechanism is general for thermal N_2 extrusion from fullerene-dihydropyrazole adducts. Finally, we note that the mechanism presented

Table 2. *First-Order Rate Constants for the Thermal N_2 Extrusion from* **2a** *in CCl_4 at Various Temperatures*

T [K]	313	323	333	340	348
$k \times 10^5$ [s^{-1}]	3.26 ± 0.06	12.5 ± 0.4	47.2 ± 2.3	134 ± 13	249 ± 52

Scheme 9. *Thermal N_2 Elimination Processes with Similar Activation Energies* [20a]



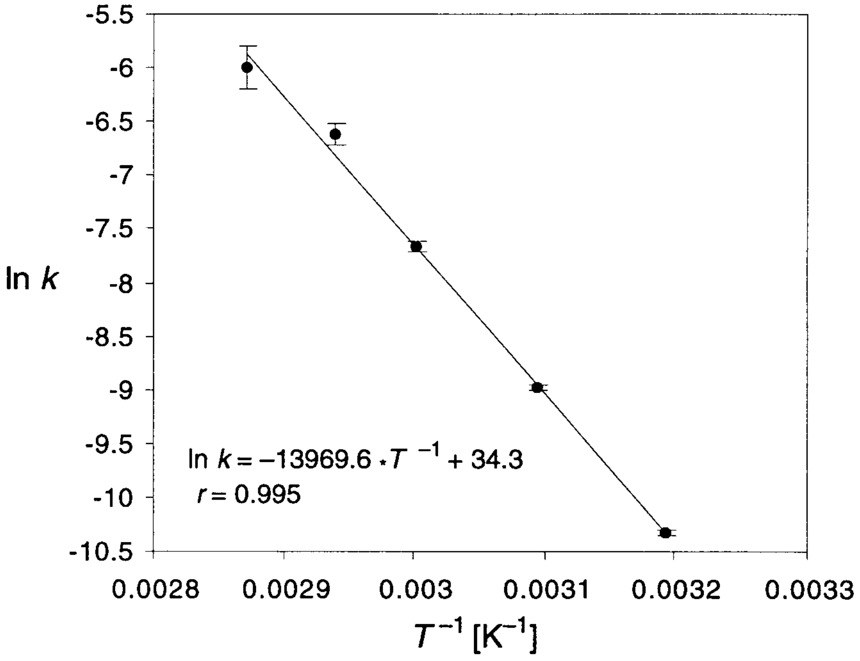


Fig. 3. Arrhenius *plot for the thermal N_2 extrusion from* **2a** *in CCl_4 between 313 and 348 K*

may well also apply to the thermal N_2 extrusion from azide adducts to C_{60}, generating 6-5 open azafullerenes, which represents the only other general reaction providing access to 6-5 open bridged fullerene derivatives [22] (for a recent theoretical treatment of this process, see [23]).

3. Conclusions. Multiple functionalization of [60]fullerene does not influence the regioselectivity of the thermal and photolytical N_2 extrusion from fullerene-pyrazolines formed by 1,3-dipolar cycloaddition of CH_2N_2. As previously observed for the CH_2N_2 adducts of pristine C_{60}, $C_{61}H_2N_2$, and C_{70}, $C_{71}H_2N_2$, thermal N_2 extrusion proceeds highly regioselectively producing 6-5 open methanofullerene derivatives, whereas photolysis of the dihydropyrazoles produces mixtures of the 6-6 closed and 6-5 open regioisomers (for a recent study on the mechanism for interconversion of these isomers, see [24]). Exploiting the confined reactivity of pentakis-adducts **1a**,**b** and **13**, together with the regioselectivity of the thermal N_2 extrusion from fullerodihydropyrazoles, allowed the synthesis of a series of novel highly functionalized hexa- to octakis-adducts of C_{60}, featuring up to three 6-5 open methano bridges. The nature of the addends in multiple adducts of C_{60} with identical addition patterns does not influence the regioselectivity of further chemical transformations. Thus, pentakis-adducts (±)-**1a**,**b**, with two fused cyclohexene and three fused cyclopropane rings, and **13**, with five fused cyclopropane rings, were transformed to heptakis-adducts with the same addition pattern upon treatment at low temperatures with CH_2N_2, followed by N_2 extrusion. The derivatives with fused cyclopropane rings, however, have only a more pronounced dipolarophile character than those with both fused cyclopropane and cyclohexene rings. According to semi-empirical calculations (AM1, PM3), the origin of this difference in reactivity is of electronic nature and is not reflected in the molecular geometry of the respective derivatives. It is noticeable, that much of the reactivity seen in this investigation could be readily predicted and/or rationalized by simple frontier orbital considerations.

The origin of the high regioselectivity of the thermal N_2 extrusion of CH_2N_2 adducts of fullerenes can be explained by a concerted, orbital-symmetry-controlled $[2\pi_s + 2\pi_s + 2\sigma_a + 2\sigma_s]$ mechanism. This mechanistic hypothesis was initially proposed based on the close similarity between the thermal and photochemical reactivity of fullerene-fused dihydropyrazoles, such as those described in this paper, and of diazoalkane adducts of toluene and xylene, which had previously been investigated by *Klärner et al.* [20]. It was further strengthened by high-level *ab initio* and density-functional calculations that supported a reaction *via* an aromatic transition state. Additional support for a common mechanism for the thermal N_2 extrusion in dihydropyrazoles fused to benzene derivatives and to fullerenes is provided by kinetic studies, which showed that the first-order reaction proceeds with similar activation energy in both classes of compounds.

This work was supported by the *Swiss National Science Foundation* and *F. Hoffmann-La Roche*, Basel. We thank Dr. *C. Thilgen*, ETH-Zürich, for assistance with the nomenclature.

Experimental Part

General. See preceding paper [9]. THF and Et_2O were distilled from Na/benzophenone, PhMe from Na immediately before use, CH_2Cl_2 from CaH_2. Anh. PhCl was dried over molecular sieves (4 Å) for several days before use. HPLC Solvents were purchased from *Biosolve*. Molecular sieves (4 Å) were activated by heating with a drying pistol to 300° for 6 h and stored in a dessicator over NaOH. Fullerene soot extract and crude fullerene-enriched soot were purchased from *MER Corporation*, Tucson, Arizona (AZ) 85706, USA. C_{60} was purified according to the procedure in [25]. Compounds **1a**,**b** [6] and **13** [7] were prepared according to literature procedures. All reactions were performed in standard glassware under an atmosphere of N_2 or Ar. Reactions involving the multiply functionalized fullerenes were conducted under strict exclusion of light and air. Degassing of solvents was performed by repetitive freeze-pump-thaw cycles or by purging with Ar before use. Evaporation and concentration *in vacuo* was done at water-aspirator pressure, and isolated solid products were dried at 10^{-1} or 10^{-7} Torr. Photolysis experiments were done with a tap-water-cooled *Pyrex* photochemical reactor with a 250-W medium-pressure Hg lamp. HPLC for kinetic measurements: *250/8/4 Nucleosil 100-7* column from *Macherey-Nagel* on an analytical *Knauer* HPLC pump *64* with *Knauer* UV detector *A0293*; wavelength: $\lambda = 310$ nm; flow rate: 2 ml min^{-1}. For FAB mass spectra of all fullerene derivatives, the experimentally observed highest peak in the molecular ion cluster is reported followed in parenthesis by the isotopic molecular formula corresponding to the calculated most intense peak in the cluster.

Kinetic Measurements. Addition of CH_2N_2 to **1a**. To a vigorously stirred soln. of **1a** (5.0 mg, 0.00338 mmol) in CH_2Cl_2 (10 ml) at 0°, an etheral soln. of CH_2N_2 (0.5 ml, *ca.* 0.76M, *ca.* 0.38 mmol) was added. Every 15 min, 20 µl of the mixture were analyzed by HPLC (CH_2Cl_2/AcOEt 99 : 1; t_R: 3.3 min (**1a**), 6.0 min (**2a**)). After 96 min, no more **1a** was detected by HPLC.

Addition of CH_2N_2 to **13**. To a vigorously stirred soln. of **13** (5.1 mg, 0.00338 mmol) in CH_2Cl_2 (10 ml) at 0°, an etheral soln. of CH_2N_2 (0.5 ml, *ca.* 0.76M, *ca.* 0.38 mmol) was added. Every 8 min, 20 µl of the mixture were analyzed by HPLC (CH_2Cl_2/AcOEt 98 : 2; t_R: 2.7 min (**13**), 5.5 min (**16**)). After 22 min, no more **13** was detected by HPLC.

Thermal N_2 Extrusion from **2a**. Vigorously stirred solns. of **2a** (5.6 mg, 0.00336 mmol) in CCl_4 (10 ml) were heated to 313, 323, 333, 340, and 348 K. Every 5 – 10 min, 20 µl of the mixture were analyzed by HPLC (CH_2Cl_2/AcOEt 99 : 1; t_R: 3.0 min ((±)-**3**), 6.0 min (**2a**)). In an independent experiment, the times it took for the soln. to reach the indicated temp. were determined. Only product distributions from that point on where included in the determination of the *Arrhenius* parameters. At the detection wavelength (310 nm), a correction factor was introduced to account for the difference in molar extinction coefficients of the respective adducts: ε((±)-**2a**) = 0.9653ε(**3a**).

*Tetraethyl 3′,3″,6′,6″-Tetrahydro-5′,3‴:5″,3‴-bis(ethano[1,4]benzenomethanoxymethano)-17′,17″-dioxo-3‴*H*,3⁗*H*,3′′′′′*H*,3′′′′′′*H*-dibenzo[21,40 : 30,31]tricyclopropa[1,9 : 16,17 : 44,45]pyrazolo[4′′′′′′,5′′′′′′:52,60](C$_{60}$-*I$_h$*)[5,6]fullerene-3⁗,3⁗,3′′′′′,3′′′′′-tetracarboxylate* (**2a**). To a soln. of **1a** (30 mg, 0.020 mmol) in $CHCl_3$ (5 ml), CH_2N_2 (2 ml, *ca.* 0.64M in Et_2O, *ca.* 60 equiv.) was added under Ar at 0°. After 90 min, the color of the soln. had changed from orange to bright-yellow. Evaporation *in vacuo* at 20°, CC (SiO_2-*H*; CH_2Cl_2), and redissolution of the residue in a minimum amount of CH_2Cl_2, followed by precipitation with pentane, afforded **2a** (22 mg, 71%). Yellow Powder. TLC (SiO_2; CH_2Cl_2): R_f 0.20. M.p. 80 – 90° (dec.). UV/VIS (CH_2Cl_2): 349 (sh, 19700), 305 (52000), 262 (44300). IR (KBr): 2978*w*, 2924*w*, 2833*w*, 1745*s*, 1615*w*, 1569*w* (N=N), 1513*w*, 1447*m*, 1367*m*, 1292*m*, 1251*s*, 1217*s*, 1095*m*, 1066*m*, 1022*m*, 967*w*, 903*w*, 852*w*, 789*m*, 764*m*, 753*m*, 708*m*, 667*w*, 588*w*, 531*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.30 – 7.05 (*m*, 8 H); 6.12 (*t*, *J* = 5.3, 2 H); 5.73 (*s*, 2 H); 5.28 (*s*, 4 H); 4.45 – 4.20 (*m*, 8 H); 3.15 – 2.80 (*m*, 16 H); 1.40 – 1.20 (*m*, 12 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 164.21; 163.98; 163.90; 163.38; 156.67; 156.37; 155.04; 153.79; 150.15; 147.72; 146.32; 145.82; 145.40; 145.35; 145.04; 144.65; 143.63; 143.50; 143.37; 142.79; 142.74; 141.77; 140.99; 140.77; 140.70; 138.55; 137.84; 131.98; 130.58; 130.53; 128.54; 125.11; 113.93; 92.02; 70.73; 69.73; 69.50; 68.84; 62.92; 62.79; 62.76; 62.06; 61.48; 57.95; 45.77; 42.26; 39.15; 34.93; 34.24; 14.21; 14.11; 14.05. FAB-MS: 1521.5 (17, M^+, $^{13}C^{12}C_{103}H_{52}O_{12}N_2^+$; calc. 1521.5), 1493.6 (100, $[M - N_2]^+$), 1479.5 (14, $[M - CH_2N_2]^+$), 720.1 (13, C_{60}^+).

*Tetrakis[(ethoxycarbonyl)methyl] 3′,3″,6′,6″-Tetrahydro-5′,3‴:5″,3‴-bis(ethano[1,4]benzenomethanoxymethano)-17′,17″-dioxo-3‴*H*,3⁗*H*,3′′′′′*H*,3′′′′′′*H*-dibenzo[21,40 : 30,31]tricyclopropa[1,9 : 16,17 : 44,45]pyrazolo[4′′′′′′,5′′′′′′:52,60](C$_{60}$-*I$_h$*)[5,6]fullerene-3⁗,3⁗,3′′′′′,3′′′′′-tetracarboxylate* (**2b**). To a soln. of **1b** (98 mg, 0.057 mmol) in $CHCl_3$ (10 ml), CH_2N_2 (3 ml; *ca.* 0.64M in Et_2O, *ca.* 35 equiv.) was added under Ar at 0°. After 90 min, the color of the soln. had changed from orange to bright-yellow. Evaporation *in vacuo* at 20°, CC (SiO_2-*H*; CH_2Cl_2/AcOEt: 50 : 1), and redissolution of the residue in a minimum amount of CH_2Cl_2, followed by precipitation with pentane, afforded **2b** (93 mg, 93%). Yellow powder. TLC (SiO_2; CH_2Cl_2/AcOEt 95 : 5): R_f 0.48. M.p. 80 – 90° (dec.). UV/VIS (CH_2Cl_2): 342 (sh, 24300), 305 (57300), 256 (51100). IR ($CHCl_3$): 3022*w*, 2933*w*, 2844*w*, 1750*s*, 1567*w* (N=N), 1450*w*, 1422*w*, 1377*m*, 1294*m*, 1189*s*, 1094*m*, 1061*m*, 1028*w*, 906*w*, 850*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.25 – 7.10 (*m*, 8 H); 6.09 (*t*, *J* = 5.0, 2 H); 5.70 (*s*, 2 H); 5.26 (br. *s*, 4 H); 4.78 (*s*, 2 H); 4.77 (*s*, 2 H); 4.72 (*s*, 2 H); 4.70 (*s*, 2 H); 4.30 – 4.10 (*m*, 8 H); 3.10 – 2.80 (br. *m*, 16 H); 1.45 – 1.15 (*m*, 12 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 166.97; 166.88; 166.83; 163.35; 163.25; 163.07; 162.98; 156.78; 156.46; 155.11;

153.92; 150.27; 147.75; 146.39; 145.93; 145.73; 145.57; 145.49; 144.79; 143.86; 143.80; 143.73; 143.60; 142.98; 142.89; 141.95; 140.91; 140.56; 140.31; 139.08 (br.); 138.83 (br.); 138.32; 137.66; 132.04; 130.66 (br.); 128.72 (br.); 125.17; 114.03; 92.17; 69.36; 69.13; 69.00; 66.58; 62.60; 62.51; 62.22; 61.90; 61.79; 61.63; 60.63; 58.09; 44.61; 45.04; 42.96; 42.41; 39.27; 35.05; 34.34; 14.34; 14.29; 14.25. FAB-MS: 1725.1 (100, $[M - N_2]^+$), 1711.4 (82, $[M - CH_2N_2]^+$).

*Tetraethyl 3′,3′′,6′,6′′-Tetrahydro-4′,3′′′′′:4′′,3′′′′′-bis(ethano[1,4]benzenomethanoxymethano)-17′,17′′-dioxo-3′′′*H,*3′′′′*H,*3′′′′′*H-*dibenzo[21,40:30,31]tricyclopropa[16,17:44,45:52,60]-1(2)a-homo(C_{60}*-I$_h$*)[5,6]fullerene-3′′′′,3′′′′,3′′′′′,3′′′′′-tetracarboxylate* ((±)-**3a**). A soln. of **2a** (22 mg, 0.0145 mmol) in CCl_4 (30 ml) was heated to reflux for 15 min, leading to a color change from yellow to orange. Subsequent CC (SiO_2-*H*; CH_2Cl_2) and redissolution of the residue in a minimum amount of CH_2Cl_2, followed by precipitation with pentane, afforded (±)-**3a** (20 mg, 93%). Orange powder. TLC (SiO_2; CH_2Cl_2): R_f 0.27. M.p. 250–260° (dec.). UV/VIS (CH_2Cl_2): 527 (sh, 1460), 498 (sh, 1620), 397 (sh, 5780), 341 (sh, 27500), 291 (56600). IR (KBr): 2979*w*, 2925*w*, 2835*w*, 1745*s*, 1616*w*, 1513*w*, 1449*m*, 1367*m*, 1290*m*, 1253*s*, 1209*s*, 1094*m*, 1064*m*, 1022*m*, 961*w*, 857*w*, 800*m*, 753*m*, 710*m*, 667*m*, 589*w*, 531*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.25–7.10 (br. *s*, 8 H); 6.21 (*t*, *J* = 5.2, 1 H); 6.19 (*t*, *J* = 5.2, 1 H); 5.14 (br. *s*, 4 H); 4.71 (*d*, *J* = 9.9, 1 H); 4.40–4.25 (*m*, 8 H); 3.35–3.25 (*m*, 4 H); 3.05–2.90 (*m*, 12 H); 2.13 (*d*, *J* = 9.9, 1 H); 1.40–1.30 (*m*, 12 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 164.05; 163.98; 163.84; 163.67; 162.67; 162.62; 156.64; 155.09; 154.81; 154.49; 154.22; 153.09; 152.69; 148.35; 147.28; 146.68; 146.59; 145.64; 145.58; 145.51; 145.44; 145.36; 143.97; 143.90; 143.62; 143.46; 143.01; 142.92; 142.74; 142.66; 142.48; 142.43; 142.26; 142.22; 141.93; 141.29; 141.05; 140.93; 140.70; 139.66; 139.39; 139.05; 138.53; 138.39; 138.36; 138.28; 137.19; 136.83; 136.72; 131.88; 131.84; 130.94; 130.26; 130.22; 128.36; 128.14; 128.03; 125.24; 124.42; 118.61; 72.40; 68.93; 68.46; 66.90; 66.47; 65.70; 64.76; 62.66; 62.61; 62.55; 62.50; 62.11; 61.96; 61.25; 51.88; 45.06; 44.13; 42.40; 42.03; 41.11; 38.96; 35.53; 34.90; 34.86; 34.33; 34.24; 14.19; 14.15; 14.14. FAB-MS: 1493.7 (100, M^+, $^{13}C^{12}C_{103}H_{52}O_{12}^+$; calc. 1493.3), 1479.6 (2, $[M - CH_2]^+$), 720.1 (2, C_{60}^+).

*Tetrakis[(ethoxycarbonyl)methyl] 3′,3′′,6′,6′′-4′,3′′′′′:4′′,3′′′′′-bis(ethano[1,4]benzenomethanoxymethano)tetrahydro-17′,17′′-dioxo-3′′′*H,*3′′′′*H,*3′′′′′*H-*dibenzo[21,40:30,31]tricyclopropa[16,17:44,45:52,60]-1(2)a-homo(C_{60}*-I$_h$*)[5,6]fullerene-3′′′′,3′′′′,3′′′′′,3′′′′′-tetracarboxylate* ((±)-**3b**). A soln. of **2b** (55 mg, 0.032 mmol) in CCl_4 (50 ml) was heated to reflux for 15 min, leading to a color change from yellow to orange. Subsequent CC (SiO_2-*H*; CH_2Cl_2/AcOEt 95:5) and redissolution of the residue in a minimum amount of CH_2Cl_2, followed by precipitation with pentane, afforded (±)-**3b** (51 mg, 93%). Orange powder. TLC (SiO_2; CH_2Cl_2/AcOEt 95:5): R_f 0.55. M.p. 230–245° (dec.). UV/VIS (CH_2Cl_2): 525 (sh, 1530), 497 (sh, 1650), 399 (sh, 1820), 359 (sh, 6670), 342 (sh, 23200), 291 (49300), 257 (sh, 51300). IR ($CHCl_3$): 2922*w*, 2855*w*, 1757*s*, 1450*w*, 1421*w*, 1379*m*, 1360*w*, 1290*m*, 1243*m*, 1185*s*, 1095*m*, 1061*m*, 1033*w*, 963*w*, 852*w*. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.25–7.10 (br. *s*, 8 H); 6.23 (*t*, *J* = 4.9, 1 H); 6.21 (*t*, *J* = 4.9, 1 H); 5.16 (br. *s*, 4 H); 4.85–4.75 (br. *m*, 9 H); 4.30–4.10 (*m*, 8 H); 3.40–3.30 (*m*, 4 H); 3.10–2.90 (*m*, 12 H); 2.15 (*d*, *J* = 9.8, 1 H); 1.35–1.20 (*m*, 12 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 166.69; 166.56; 166.51; 163.02; 162.87; 162.71; 162.58; 162.52; 156.68; 155.06; 154.85; 154.51; 154.28; 153.12; 152.73; 148.30; 147.35; 146.84; 146.73; 145.67; 145.62; 145.54; 145.40; 144.07; 143.75; 143.58; 143.52; 143.06; 142.78; 142.60; 142.50; 142.42; 142.26; 141.98; 141.73; 141.48; 141.39; 141.15; 141.01; 140.74; 140.66; 140.44; 139.68; 139.50; 139.10; 138.95; 138.44; 138.14; 137.88; 137.22; 137.07; 136.25; 131.90; 131.81; 131.77; 130.97; 130.26; 128.43; 128.27; 128.19; 125.22; 124.59; 118.80; 71.89; 68.68; 68.52; 68.43; 66.86; 66.44; 65.27; 64.35; 62.54; 62.36; 62.27; 62.16; 62.12; 61.99; 61.65; 61.55; 61.51; 61.28; 51.93; 43.81; 42.96; 42.43; 42.05; 41.08; 38.94; 35.41; 34.92; 34.88; 34.28; 34.20; 14.14; 13.96. FAB-MS: 1725.1 (100, M^+, $^{13}C^{12}C_{111}H_{60}O_{20}^+$; calc. 1725.4), 719.8 (62, C_{60}^+).

*Tetraethyl 3′,3′′,6′,6′′-Tetrahydro-5′,3′′′:5′′,3′′′-bis(ethano[1,4]benzenomethanoxymethano)-17′,17′′-dioxo-3′′′*H,*3′′′′*H,*3′′′′′*H,*3′′′′′′*H-*dibenzo[1,9:52,60]tetracyclopropa[16,17:21,40:30,31:44,45](C_{60}*-I$_h$*)[5,6]fullerene-3′′′′,3′′′′,3′′′′′,3′′′′′-tetracarboxylate* (**4**). Solns. of **2a** in C_6D_6 (9.6 mM) in an NMR tube were held close to a *Pyrex* photolysis vessel containing a medium pressure Hg lamp and were photolyzed for *ca.* 8 min. During the photolysis, the mixture was repeatedly cooled (*ca.* every 1.5 min) by holding the NMR tube in ice-water for *ca.* 15 s. CC (SiO_2-*H*; CH_2Cl_2) afforded **4** and (±)-**3a** in a combined yield between 9 and 21%. Subsequent addition of CH_2N_2 at 0° to the product mixture in CH_2Cl_2 (25 ml) led to an immediate color change from orange to yellow. CC (SiO_2-*H*; CH_2Cl_2) and redissolution of the residue in a minimum amount of CH_2Cl_2, followed by precipitation with pentane, afforded **4**. Bright-yellow solid. TLC (SiO_2; CH_2Cl_2): R_f 0.27. M.p. > 260°. UV/VIS (CH_2Cl_2): 357 (sh, 16300), 309 (sh, 49900), 287 (58600). IR (CH_2Cl_2): 2961*w*, 2928*w*, 2853*w*, 1740*s*, 1465*w*, 1450*w*, 1368*m*, 1294*m*, 1256*s*, 1096*m*, 1078*m*, 1065*m*, 1020*m*, 859*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.10–7.10 (br. *m*, 8 H); 6.10 (*t*, *J* = 5.3, 2 H); 5.14 (br. *s*, 4 H); 4.26 (*q*, *J* = 7.1, 4 H); 4.20 (*q*, *J* = 7.1, 4 H); 3.14 (*d*, *J* = 5.3, 4 H); 2.95–2.80 (*m*, 12 H); 2.57 (*s*, 2 H); 1.27 (*t*, *J* = 7.1, 6 H); 1.21 (*t*, *J* = 7.1, 6 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 163.99; 163.74; 163.11; 156.20; 154.87; 145.51; 145.41; 143.50; 143.15; 142.78; 142.53; 140.33; 139.82; 138.91; 131.81; 130.25;

128.28; 125.15; 71.12; 68.54; 63.57; 62.54; 62.51; 61.98; 61.73; 46.10; 42.28; 39.66; 34.87; 34.32; 14.16; 14.08. FAB-MS: 1493.7 (100, M^+, $^{13}C^{12}C_{103}H_{52}O_{12}^+$; calc. 1493.3), 720.1 (3, C_{60}^+).

*Tetraethyl 3′,3″,6′,6″-Tetrahydro-4′,3′′′′′:4″,3′′′′′′-bis(ethano[1,4]benzenomethanoxymethano)-17′,17″-dioxo-3‴*H*,3′′′′*H*,3′′′′′*H*-dibenzo[21,40 :30,31]tricyclopropa[16,17:44,45 :52,60]-1(2)a,1(5)a,8(9)a-trihomo(C$_{60}$-*I$_h$*)[5,6]fullerene-3‴,3‴,3′′′′,3′′′′-tetracarboxylate* ((±)-**5a**). To a soln. of (±)-**3a** (25 mg, 0.0167 mmol) in $CHCl_3$ (5 ml), CH_2N_2 (2 ml; *ca.* 0.64M in Et_2O, *ca.* 75 equiv.) was added under Ar at 0°. The mixture was stirred at 0° for 10 min. Within 1 min, the color of the soln. had changed from orange to orange-yellow. Evaporation, CC (SiO_2-*H*; CH_2Cl_2), and redissolution of the residue in a minimum amount of CH_2Cl_2, followed by precipitation with pentane, afforded (±)-**5a** (22 mg, 85%). TLC (SiO_2; CH_2Cl_2): R_f 0.35. M.p. 215 – 235° (dec.). UV/VIS (CH_2Cl_2): 303 (sh), 286. ^1H-NMR (500 MHz, $CDCl_3$): ^1H-NMR (500 MHz, $CDCl_3$): 7.30-7.10 (*m*, 8 H); 6.07 (*t*, $J = 5.3$, 1 H); 6.03 (*t*, $J = 5.3$, 1 H); 5.30 – 5.20 (br. *m*, 4 H); 4.48 (*d*, $J = 15.3$, 1 H); 4.41 (*d*, $J = 15.1$, 1 H); 4.42 – 4.37 (*m*, 2 H); 4.30 – 4.15 (*m*, 6 H); 4.06 (*d*, $J = 10.0$, 1 H); 3.39 (*d*, $J = 15.3$, 1 H); 3.37 (*d*, $J = 15.1$, 1 H); 3.15 – 2.85 (*m*, 12 H); 2.80 (*d*, $J = 14.1$, 2 H); 2.71 (*d*, $J = 14.1$, 2 H); 2.04 (*d*, $J = 10.0$, 1 H); 1.40 (*t*, $J = 7.1$, 3 H); 1.30 – 1.20 (*m*, 9 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 164.16; 164.08; 163.98; 163.70; 163.36; 162.90; 157.93; 154.96; 154.70; 154.36; 153.19; 151.93; 147.76; 145.77; 145.66; 145.49; 145.38; 145.16; 144.91; 144.71; 144.49; 144.06; 143.56; 143.35; 143.09; 142.75; 142.58; 142.50; 142.22; 141.51; 140.84; 140.78; 140.73; 139.90; 139.30; 139.24; 139.13; 138.69; 137.94; 137.69; 137.31; 136.17; 135.67; 134.61; 134.30; 132.76; 131.90; 131.87; 131.58; 131.42; 130.36; 130.29; 129.61; 128.64; 128.10; 126.02; 125.12; 124.76; 115.77; 70.98; 68.61; 68.49; 66.20; 66.04; 62.58; 62.53; 62.44; 62.34; 62.01; 61.11; 60.90; 60.84; 58.32; 47.25; 46.23; 45.50; 43.85; 42.47; 41.97; 40.91; 40.58; 37.80; 37.63; 34.86; 34.75; 34.70; 34.23; 14.24; 14.13; 14.06. FAB-MS: 1521.2 (100, M^+, $^{13}C^{12}C_{105}H_{56}O_{12}^+$; calc. 1521.4), 1507.5 (13, $[M - CH_2]^+$), 1493.3 (15, $[M - 2\ CH_2]^+$).

*Tetrakis[(ethoxycarbonyl)methyl] 3′,3″,6′,6″-Tetrahydro-4′,3′′′′′:4″,3′′′′′′-bis(ethano[1,4]benzenomethanoxymethano)17′,17″-dioxo-3‴*H*,3′′′′*H*,3′′′′′*H*-dibenzo[21,40 :30,31]tricyclopropa[16,17:44,45 :52,60]-1(2)a,1(5)a,8(9)a-trihomo(C$_{60}$-*I$_h$*)[5,6]fullerene-3‴,3‴,3′′′′,3′′′′-tetracarboxylate* ((±)-**5b**). To a soln. of (±)-**3b** (75 mg, 0.044 mmol) in $CHCl_3$ (10 ml), CH_2N_2 (3 ml; *ca.* 0.64M in Et_2O, *ca.* 40 equiv.) was added under Ar at 0°. The mixture was stirred at 0° for 10 min. Within 1 min, the color of the soln. had changed from orange to yellow. Evaporation, CC (SiO_2-*H*; $CH_2Cl_2 \rightarrow CH_2Cl_2$/AcOEt 98 :2), and redissolution of the residue in a minimum amount of $CHCl_3$, followed by precipitation with cyclohexane, afforded (±)-**5b** (69 mg, 90%). M.p. 200 – 215° (dec.). UV/VIS (CH_2Cl_2): 303 (sh, 48700), 286 (51500). IR ($CHCl_3$): 2958*w*, 2925*w*, 2856*w*, 1750*s*, 1602*w*, 1451*w*, 1422*w*, 1381*m*, 1360*w*, 1293*m*, 1275*m*, 1257*m*, 1190*s*, 1096*m*, 1061*w*, 1021*w*, 919*w*, 853*w*. ^1H-NMR (500 MHz, $CDCl_3$): 7.30 – 7.10 (*m*, 8 H); 6.07 (*t*, $J = 5.3$, 1 H); 6.02 (*t*, $J = 5.3$, 1 H); 5.30 – 5.20 (br. *m*, 4 H); 4.84 (*s*, 2 H); 4.75 – 4.55 (*m*, 6 H); 4.53 (*d*, $J = 15.6$, 1 H); 4.46 (*d*, $J = 15.2$, 1 H); 4.30 – 4.20 (*m*, 2 H); 4.28 (*q*, $J = 7.1$, 2 H); 4.20 (*q*, $J = 7.1$, 2 H); 4.13 (*q*, $J = 7.1$, 2 H); 4.10 (*d*, $J = 10.5$, 1 H); 3.49 (*d*, $J = 15.6$, 1 H); 3.38 (*d*, $J = 15.2$, 1 H); 3.15 – 2.85 (*m*, 12 H); 2.81 (*d*, $J = 14.1$, 2 H); 2.71 (*d*, $J = 14.1$, 2 H); 2.02 (*d*, $J = 10.2$, 1 H); 1.31 (*t*, $J = 7.1$, 3 H); 1.30 (*t*, $J = 7.1$, 3 H); 1.25 (*t*, $J = 7.1$, 3 H); 1.18 (*t*, $J = 7.1$, 3 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 166.76; 166.69; 166.66; 166.56; 163.61; 163.27; 163.22; 163.06; 163.01; 162.05; 157.93; 154.93; 154.73; 154.41; 153.21; 151.97; 147.81; 146.42; 146.17; 145.86; 145.77; 145.70; 145.43; 145.40; 144.93; 144.71; 144.66; 144.30; 144.09; 143.71; 143.46; 143.22; 143.16; 143.00; 142.78; 142.71; 142.50; 142.43; 140.97; 140.86; 140.82; 140.47; 139.75; 139.48; 139.33; 138.79; 138.72; 138.20; 138.05; 137.30; 136.90; 136.27; 135.64; 134.70; 134.55; 132.66; 132.45; 131.97; 131.84; 131.79; 130.40; 130.28; 129.47; 128.74; 128.15; 126.34; 125.09; 124.80; 116.88; 70.52; 68.66; 68.54; 68.03; 66.75; 66.14; 65.46; 62.60; 62.26; 62.20; 62.02; 61.89; 61.64; 61.56; 61.46; 61.42; 61.12; 60.88; 60.63; 58.35; 47.37; 46.28; 44.16; 42.61; 42.47; 41.97; 40.89; 40.53; 37.76; 34.90; 34.74; 34.64; 34.18; 14.20; 14.17; 14.12; 14.01. FAB-MS: 1753.3 (100, M^+, $^{13}C^{12}C_{113}H_{64}O_{20}^+$; calc. 1753.4), 1739.1 (12, $[M - CH_2]^+$), 719.9 (31, C_{60}^+).

*Tetraethyl 3′,3″,6′,6″-Tetrahydro-4′,3′′′′′:4″,3′′′′′′-bis(ethano[1,4]benzenomethanoxymethano)-17′,17″-dioxo-3‴*H*,3′′′′*H*,3′′′′′*H*-dibenzo[21,40 :30,31]tricyclopropa[16,17:44,45 :52,60] -1(2)a,1(5)a-dihomo(C$_{60}$-*I$_h$*)[5,6]fullerene-3‴,3‴,3′′′′,3′′′′-tetracarboxylate* (**6a**). To a soln. of (±)-**3a** (81 mg, 0.054 mmol) in CH_2Cl_2 (20 ml), CH_2N_2 (3 ml, *ca.* 0.64M in Et_2O, *ca.* 40 equiv.) was added at – 80°. The cooling bath was subsequently removed, and once the temp. of the mixture reached – 60° (after *ca.* 10 min), AcOH (3 ml) was added. Concentration *in vacuo*, CC (SiO_2-*H*; CH_2Cl_2/AcOEt 98 :2), and redissolution of the residue in a minimum amount of CH_2Cl_2, followed by precipitation with hexane, afforded **6a** (67 mg, 82%). Yellow powder. M.p. 230 – 240° (dec.). UV/VIS (CH_2Cl_2): 395 (sh, 14900), 365 (sh, 26100), 349 (sh, 36200), 315 (sh, 67000), 296 (80000), 252 (sh, 80700). IR (KBr): 2923*m*, 1746*s*, 1634*m*, 1445*m*, 1367*m*, 1249*s*, 1216*m*, 1062*m*, 798*w*, 536*m*, 457*w*. ^1H-NMR (400 MHz, $CDCl_3$): 7.20 – 7.10 (br. *m*, 8 H); 6.13 (*t*, $J = 5.3$, 2 H); 5.22 (br. *s*, 4 H); 4.44 (*d*, $J = 10.9$, 2 H); 4.37 (*q*, $J = 7.1$, 2 H); 4.35 – 4.20 (*m*, 6 H); 3.22 (*dd*, $J = 14.2$, 5.4, 2 H); 3.16 (*dd*, $J = 14.2$, 5.4, 2 H); 3.05 – 2.85 (*m*, 12 H); 2.76 (*d*, $J = 10.9$, 2 H); 1.38 (*t*, $J = 7.1$, 3 H); 1.32 (*t*, $J = 7.1$, 3 H); 1.26 (*t*, $J = 7.1$, 6 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 164.26; 164.14; 163.78; 162.90 (2 x); 156.57; 153.94; 153.30; 146.76; 146.53; 146.30; 145.72; 145.53; 145.41; 144.36; 144.21;

143.62; 142.68; 142.47; 141.63; 141.18; 140.45; 140.12; 138.61; 138.37; 136.92; 134.51; 133.76; 131.90; 131.00; 130.34; 130.30; 128.24; 125.11; 116.45; 68.52; 67.26; 66.13; 62.53; 62.50; 62.41; 62.25; 61.63; 61.54; 61.33; 47.92; 45.04; 44.70; 42.19; 40.69; 34.89; 34.24; 14.23; 14.16; 14.12; 14.09. FAB-MS: 1507.5 (100, M^+, $^{13}C^{12}C_{104}H_{54}O_{12}^+$; calc. 1507.6), 1493.5 (16, $M - CH_2]^+$), 1479.2 (8, $[M - 2\ CH_2]^+$), 1462.4 (10, $[M - C_2H_5O]^+$), 720.0 (C_{60}^+).

*Tetrakis[(ethoxycarbonyl)methyl] 3',3'',6',6''-Tetrahydro-4',3''''':4'',3'''''-bis(ethano[1,4]benzenomethanoxymethano)-17',17''-dioxo-3'''*H*,3''''*H*,3'''''*H*-dibenzo[21,40:30,31]tricyclopropa[16,17:44,45:52,60]-1(2)a,1(5)a-dihomo(C_{60}-*I$_h$*)[5,6]fullerene-3''',3''',3'''',3''''-tetracarboxylate* (**6b**). To a soln. of (±)-**3b** (150 mg, 0.087 mmol) in CH_2Cl_2 (10 ml), CH_2N_2 (3 ml, *ca.* 0.64M in Et_2O; *ca.* 20 equiv.) was added at –80°. The cooling bath was subsequently removed, and once the temp. of the mixture reached –60° (after *ca.* 10 min), AcOH (3 ml) was added. Concentration *in vacuo*, CC (SiO_2-*H*; CH_2Cl_2/AcOEt 95:5), and redissolution of the residue in a minimum amount of CH_2Cl_2, followed by precipitation with pentane, afforded **6b** (119 mg, 79%). Yellow powder. TLC (SiO_2; CH_2Cl_2): R_f 0.21. M.p. 195–210° (dec.). UV/VIS (CH_2Cl_2): 393 (sh, 7040), 348 (sh, 24400), 317 (sh, 51500), 299 (58100), 250 (sh, 52600). IR (KBr): 2923*w*, 1750*s*, 1450*w*, 1422*w*, 1396*w*, 1379*m*, 1285*m*, 1251*m*, 1193*s*, 1092*m*, 1060*m*, 1033*m*, 964*w*, 852*w*, 797*w*, 769*w*, 754*w*, 716*w*, 589*w*, 571*w*, 546*w*, 535*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.20–7.05 (*m*, 8 H); 6.14 (*t*, $J = 5.4$, 2 H); 5.21 (br. *s*, 4 H); 4.81 (*s*, 2 H); 4.75 (*s*, 2 H); 4.73 (*s*, 2 H); 4.71 (*s*, 2 H); 4.48 (*d*, $J = 10.9$, 2 H); 4.26 (*q*, $J = 7.1$, 2 H); 4.22 (*q*, $J = 7.1$, 2 H); 4.21 (*q*, $J = 7.1$, 2 H); 4.15 (*q*, $J = 7.1$, 2 H); 3.21 (*dd*, $J = 14.2, 5.4$, 2 H); 3.15 (*dd*, $J = 14.2, 5.4$, 2 H); 3.05–2.85 (*m*, 12 H); 2.75 (*d*, $J = 10.9$, 2 H); 1.30 (*t*, $J = 7.1$, 3 H); 1.27 (*t*, $J = 7.1$, 3 H); 1.26 (*t*, $J = 7.1$, 3 H); 1.20 (*t*, $J = 7.1$, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 166.74; 166.67; 166.62; 166.57; 163.29; 163.12; 163.04; 162.81; 162.78; 156.58; 153.94; 153.34; 146.86; 146.47; 146.39; 145.76; 145.61; 145.54; 144.37; 144.29; 143.73; 142.76; 142.70; 142.46; 141.19; 141.14; 140.48; 139.62; 139.50 (br.); 138.39 (br.); 138.05; 137.96; 136.95; 134.75; 133.77; 131.81; 131.46; 130.33; 130.30; 125.07; 116.63; 68.55; 68.09; 67.17; 66.05; 62.24; 62.18; 62.05; 61.63; 61.60; 61.57; 61.49; 61.41; 61.33; 61.16; 47.94; 44.96; 43.55; 42.87; 42.18; 40.64; 34.89; 34.75; 14.18; 14.13; 14.10; 14.04. FAB-MS: 1739.1 (100, M^+, $^{13}C^{12}C_{112}H_{62}O_{20}^+$; calc. 1739.4), 1725.1 (7, $[M - CH_2]^+$), 1711.3 (3, $[M - 2\ CH_2]^+$), 719.8 (7, C_{60}^+).

*Tetraethyl 1,3',3'',6',6'',9-Hexahydro-1,9-dihydroxy-4',3''''':4'',3'''''-bis(ethano[1,4]benzenomethanoxymethano)-17',17''-dioxo-3'''*H*,3''''*H*,3'''''*H*-dibenzo[21,40:30,31]tricyclopropa[16,17:44,45:52,60]-1(2)a,1(5)a-dihomo(C_{60}-*I$_h$*)[5,6]fullerene-3''',3''',3'''',3''''-tetracarboxylate* (**14**). To a degassed soln. of **6a** (52 mg, 0.035 mmol) in CH_2Cl_2 (50 ml), an aq. soln. of $KMnO_4$ and [18]crown-6 (3.8 ml, 0.01M $KMnO_4$; 0.01M [18]crown-6) was added at 20°. After 2 h, AcOH (5 ml) was added, and the mixture was stirred for 2 h at 20°. Sat. aq. $NaHCO_3$ soln. was added, and the mixture was filtered. The org. phase was washed with sat. aq. $NaHCO_3$ soln., sat. aq. NaCl soln., and H_2O (2 ×). The aq. phase was re-extracted with CH_2Cl_2, and the combined org. phases were dried (Na_2SO_4). CC (SiO_2-*H*; CH_2Cl_2/AcOEt 7:3), evaporation *in vacuo*, and redissolution of the residue in a minimum amount of CH_2Cl_2, followed by precipitation with pentane, afforded **14** (35 mg, 66%). Bright-yellow solid. TLC (SiO_2; CH_2Cl_2/AcOEt 90:10): R_f 0.32. M.p. 186–192° (dec.). UV/VIS (CH_2Cl_2): 425 (sh, 3290), 348 (sh, 24500), 313 (sh, 55100), 297 (62900), 259 (sh, 46300). IR (CCl_4): 3734*w*, 3396*w*, 2981*w*, 2960*w*, 2929*w*, 2872*w*, 2851*w*, 1746*s*, 1652*w*, 1615*w*, 1514*w*, 1450*m*, 1367*w*, 1244*s*, 1095*m*, 1065*m*, 1024*m*, 976*w*, 911*w*, 858*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.25–7.09 (br. *m*, 8 H); 6.01 (*t*, $J = 5.3$, 2 H); 5.31 (*s*, 4 H); 4.66 (br. *s*, 1 H); 4.40–4.20 (br. *s*, 1 H); 4.33 (*q*, $J = 7.1$, 2 H); 4.31 (*q*, $J = 7.1$, 2 H); 4.19 (*q*, $J = 7.1$, 4 H); 3.84 (br. *d*, $J = 11.6$, 2 H); 3.62 (br. *d*, $J = 11.6$, 2 H); 2.91–2.84 (br. *m*, 14 H); 1.34 (*t*, $J = 7.1$, 3 H); 1.33 (*t*, $J = 7.1$, 3 H); 1.25 (*t*, $J = 7.1$, 6 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 164.68; 164.23; 164.22; 163.56; 163.30; 158.05; 156.77; 151.48; 149.88; 148.49; 147.82; 146.43; 145.73; 145.17; 144.86; 144.68; 144.02; 143.53; 143.21; 142.79; 142.55; 141.64; 141.59; 140.99; 138.91; 138.33; 136.93; 135.06; 134.43; 133.08; 132.03; 130.64; 130.56; 128.52; 124.93; 84.40; 68.81; 69.94; 62.63; 62.59; 62.37; 61.63; 61.11; 60.99; 60.33; 49.85; 42.15; 40.34; 34.88; 34.17; 14.18; 14.08. FAB-MS: 1541.6 (100, M^+, $^{13}C^{12}C_{104}H_{56}O_{14}^+$; calc. 1541.6), 1525.3 (26, $[M - OH]^+$), 1523.1 (45, $[M - H_2O]^+$), 1495.1 (16, $[M - C_2H_5O]^+$), 1382.7 (9, $[M - C(CO_2CH_2CH_3)_2]^+$), 1225.0 (5, $[M - 2\ C(CO_2CH_2CH_3)_2]^+$), 719.8 (7, C_{60}^+).

*Decaethyl 3'*H*,3''*H*,3'''*H*,3''''*H*,3'''''*H*,3''''''*H*-Pentacyclopropa[1,9:16,17:21,40:30,31:44,45]pyrazolo[4'''''',5'''''':52,60](C_{60}-*I$_h$*)[5,6]fullerene-3',3',3'',3'',3''',3''',3'''',3'''',3''''',3'''''-decacarboxylate* (**16**). To a soln. of **13** (130 mg, 0.086 mmol) in CH_2Cl_2 (20 ml), CH_2N_2 (3 ml; *ca.* 0.64M in Et_2O, *ca.* 20 equiv.) was added under Ar at 0°. After 20 min, the color of the soln. had changed from orange to bright-yellow. Evaporation *in vacuo* at 20° and redissolution of the residue in a minimum amount of CH_2Cl_2, followed by precipitation with pentane, afforded **16** (125 mg, 94%). Yellow powder. TLC (SiO_2; CH_2Cl_2): R_f 0.20. M.p. 96–103° (dec.). UV/VIS (CH_2Cl_2): 579 (sh), 544, 508 (sh), 459, 415, 385, 297, 277. IR (KBr): 2981*m*, 2932*m*, 1743*s*, 1636*w*, 1571*w*, 1464*w*, 1368*w*, 1239*s*, 1095*m*, 1022*m*, 859*w*, 800*m*, 713*w*, 539*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.95 (*s*, 2 H); 4.45–4.20 (*m*, 20 H); 1.43–1.27 (*m*, 30 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 163.21; 163.02; 162.93; 162.83; 150.86; 146.45; 145.85; 145.25; 145.12; 145.06; 144.90; 144.80; 144.74; 144.61; 144.30; 143.06; 142.61; 141.44; 141.22; 141.12; 140.90; 140.74; 139.98; 139.63; 139.53; 139.19; 138.39; 114.84; 91.03; 68.97; 68.40; 67.20; 67.01; 61.99; 58.82; 44.69; 44.54;

44.21; 41.20; 13.04. FAB-MS: 1553.3 (63, M^+, $^{12}C_{95}{}^{13}CH_{52}O_{20}N_{12}^+$; calc. 1553.3), 1539.3 (100, $[M - N]^+$), 1525.4 (29, $[M - N_2]^+$), 1508.3 (19, $[M - C_2H_5O]^+$), 1495.3 (29, $[M - N_{2-}C_2H_5O]^+$), 1395.4 (30, $[M - C(CO_2CH_2CH_3)_2]^+$), 720.1 (28, C_{60}^+).

Decaethyl 3′H,3″H,3‴H,3′′′′H,3′′′′′H-Pentacyclopropa[16,17:21,40:30,31:44,45:52,60]-1(2)a-homo(C_{60}-I_h)[5,6]fullerene-3′,3′,3″,3″,3‴,3‴,3′′′′,3′′′′,3′′′′′,3′′′′′-decacarboxylate ((±)-**17**). A soln. of **16** (59 mg, 0.038 mmol) in $CHCl_3$ (5 ml) was heated to reflux for 5 h, leading to a color change from yellow to orange. CC (SiO_2-*H*; CH_2Cl_2/AcOEt 9:1), and redissolution of the residue in a minimum amount of CH_2Cl_2, followed by precipitation with pentane, afforded (±)-**17** as an orange powder (40 mg, 82%). Red-orange powder. TLC (SiO_2; CH_2Cl_2): R_f 0.32. M.p. > 250° (dec.). UV/VIS (CH_2Cl_2): 540 (sh, 1500), 517 (1720), 414 (sh, 3340), 348 (sh, 20700), 322 (sh, 39700), 287 (69800), 245 (77900). IR (KBr): 2980*w*, 2931*w*, 1744*s*, 1465*w*, 1446*w*, 1390*w*, 1389*w*, 1367*m*, 1257*s*, 1219*s*, 1095*m*, 1079*m*, 1020*m*, 858*w*, 814*w*, 717*m*, 544*m*, 529*m*, 519*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.24 (*d*, $J = 9.9$, 1 H); 4.45 – 4.25 (*m*, 20 H); 2.45 (*d*, $J = 9.9$, 1 H); 1.45 – 1.29 (*m*, 30 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 164.08; 164.05; 163.96 (2 ×); 163.93; 163.87; 163.85; 163.57; 163.49; 163.40; 147.61; 147.29; 146.67; 146.54; 146.24; 146.11; 145.99; 145.73; 145.69; 145.00; 144.66; 144.41; 144.38; 143.34; 142.99; 142.75; 142.69; 142.47; 141.93; 141.51; 141.41; 141.36; 141.26; 141.23; 140.92; 140.58; 140.08; 139.96; 139.78; 139.67; 139.55; 139.25; 139.00; 137.56; 135.08; 134.66; 132.93; 131.43; 124.95; 119.29; 70.62; 70.01; 69.64; 69.47; 69.02; 68.57; 67.26; 64.48; 63.17; 62.85; 62.82; 62.68; 62.64; 52.19; 46.16; 45.78; 44.56; 43.87; 35.6; 14.15; 14.02; 14.07; 14.05; 13.99. FAB-MS: 1525.1 (100, M^+, $^{13}C^{12}C_{95}H_{52}O_{20}^+$; calc. 1525.3), 1480.1 (23, $[M - C_2H_5O]^+$), 1366.0 (5, $[M - C(CO_2CH_2CH_3)_2]^+$), 719.8 (26, C_{60}^+).

Decaethyl 3′H,3″H,3‴H,3′′′′H,3′′′′′H-Pentacyclopropa[16,17:21,40:30,31:44,45:52,60]-1(2)a,1(5)a-dihomo(C_{60}-I_h)[5,6]fullerene-3′,3′,3″,3″,3‴,3‴,3′′′′,3′′′′,3′′′′′,3′′′′′-decacarboxylate (**18**). To a soln. of (±)-**17** (108 mg, 0.071 mmol) in CH_2Cl_2 (10 ml), CH_2N_2 (3 ml, *ca.* 0.64M in Et_2O; ca. 25 equiv.) was added at − 80°. The cooling bath was subsequently removed, and once the temp. of the mixture reached − 60°, the reaction was quenched immediately with AcOH (4 ml). Evaporation *in vacuo* and redissolution of the residue in a minimum amount of CH_2Cl_2, followed by precipitation with hexane, afforded **18** (107 mg, 98%). Yellow powder. TLC (SiO_2; CH_2Cl_2): R_f 0.28. M.p. 210 – 220° (dec.). UV/VIS (CH_2Cl_2): 346 (sh, 28300), 318 (sh, 46700), 288 (71100), 249 (76000). IR (KBr): 2980*w*, 2934*w*, 1744*s*, 1558*w*, 1465*m*, 1445*m*, 1390*m*, 1368*m*, 1296*m*, 1256*s*, 1220*s*, 1095*m*, 1078*m*, 1034*m*, 860*w*, 720*w*, 544*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 4.80 (*d*, $J = 10.9$, 2 H); 4.40 – 4.20 (*m*, 20 H); 3.02 (*d*, $J = 10.9$, 2 H); 1.35 – 1.25 (*m*, 30 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 164.31; 164.13; 164.06; 164.01; 163.81; 163.74; 163.63; 147.26; 146.70; 145.93; 145.89; 145.72; 145.52; 145.45; 145.02; 143.98; 143.29; 143.07; 142.58; 141.49; 141.43; 141.36; 140.43; 140.13; 140.03; 139.72; 139.58; 139.43; 135.88; 133.79; 133.75; 132.31; 117.34; 70.19; 69.26; 69.02; 68.19; 66.98; 62.76; 62.71; 62.69; 62.62; 62.34; 60.32; 45.63; 45.30; 44.45; 43.52; 14.09; 14.04; 14.01; 13.97. FAB-MS: 1539.1 (100, M^+, $^{13}C^{12}C_{96}H_{54}O_{20}^+$; calc. 1539.3), 1525.1 (7, $[M - CH_2]^+$), 1511.1 (4, $[M - 2\ CH_2]^+$), 1494.1 (29, $[M - C_2H_5O]^+$), 1380.0 (5, $[M - C(CO_2CH_2CH_3)_2]^+$), 719.8 (16, C_{60}^+).

Decaethyl 1,9-Dihydro-1,9-dihydroxy-3′H,3″H,3‴H,3′′′′H,3′′′′′H-pentaclopropa[16,17:21,40:30,31:44,45:52,60]-1(2)a,1(5)a-dihomo(C_{60}-I_h)[5,6]fullerene-3′,3′,3″,3″,3‴,3‴,3′′′′,3′′′′,3′′′′′,3′′′′′-decacarboxylate (**19**). To a soln. of **18** (30 mg, 0.019 mmol) in CH_2Cl_2 (30 ml), an aq. soln. of $KMnO_4$ and [18]crown-6 (2.5 ml, 0.01M $KMnO_4$; 0.01M [18]crown-6) was added at 20°. After 3 h, AcOH (3 ml) was added, and the mixture was stirred for 2 h at 20°. Sat. aq. $NaHCO_3$ soln. was added, and the mixture was filtered. The org. phase was washed with sat. aq. $NaHCO_3$ soln., sat. aq. NaCl soln., and H_2O (2 ×). The aq. phase was re-extracted with CH_2Cl_2, and the combined org. phases were dried (Na_2SO_4). CC (SiO_2-*H*; CH_2Cl_2/AcOEt 1:1), evaporation, and redissolution of the residue in a minimum amount of CH_2Cl_2, followed by precipitation with pentane, afforded **19** (26 mg, 85%). Bright-yellow solid. TLC (SiO_2; AcOEt) R_f 0.8. IR ($CHCl_3$): 3606*m*, 3465*w*, 3008*m*, 1739*s*, 1602*s*, 1256*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.89 (br. *s*, 2 H); 4.50 – 4.15 (*m*, 22 H); 3.91 (*d*, $J = 11.6$, 2 H). FAB-MS: 1573.2 (84, M^+, $^{13}C^{12}C_{96}H_{56}O_{22}^+$; calc. 1573.3), 1556.4 (50, $[M - H_2O]^+$), 1539.3 (10, $[M - 2\ OH]^+$), 1528.4 (24, $[MH - C_2H_5O]^+$), 1527.3 (28, $[M - C_2H_5O]^+$), 1510.5 (10, $[M - H_2O - C_2H_5O]^+$), 1417.1 (7, $[M - C(CO_2CH_2CH_3)_2]^+$), 719.9 (40, C_{60}^+).

REFERENCES

[1] T. Suzuki, Q. Li, K. C. Khemani, F. Wudl, *J. Am. Chem. Soc.* **1992**, *114*, 7301.

[2] a) A. B. Smith III, R. M. Strongin, L. Brard, G. T. Furst, W. J. Romanow, K. G. Owens, R. J. Goldschmidt, *J. Chem. Soc., Chem. Commun.* **1994**, 2187; b) A. B. Smith III, R. M. Strongin, L. Brard, G. T. Furst, W. J. Romanow, K. G. Owens, R. J. Goldschmidt, R. C. King, *J. Am. Chem. Soc.* **1995**, *117*, 5492.

[3] E. Vogel, *Pure Appl. Chem.* **1993**, *65*, 143.

[4] a) F. Cardullo, P. Seiler, L. Isaacs, J.-F. Nierengarten, R. F. Haldimann, F. Diederich, T. Mordasini-Denti, W. Thiel, C. Boudon, J.-P. Gisselbrecht, M. Gross, *Helv. Chim. Acta* **1997**, *80*, 343; b) C. Boudon, J.-P. Gisselbrecht, M. Gross, L. Isaacs, H. L. Anderson, R. Faust, F. Diederich, *Helv. Chim. Acta* **1995**, *78*, 1334.

[5] R. F. Haldimann, F.-G. Klärner, F. Diederich, *Chem. Commun.* **1997**, 237.

[6] L. Isaacs, F. Diederich, R. F. Haldimann, *Helv. Chim. Acta* **1997**, *80*, 317.

[7] I. Lamparth, A. Herzog, A. Hirsch, *Tetrahedron* **1996**, *52*, 5065.

[8] A. Hirsch, I. Lamparth, H. R. Karfunkel, *Angew. Chem.* **1994**, *106*, 453; *Angew. Chem., Int. Ed.* **1994**, *33*, 437; F. Djojo, A. Hirsch, *Chem. Eur. J.* **1998**, *4*, 344.

[9] J.-P. Bourgeois, C. R. Woods, F. Cardullo, T. Habicher, J.-F. Nierengarten, R. Gehrig, F. Diederich, *Helv. Chim. Acta* **2001**, *84*, 1207.

[10] L. Isaacs, A. Wehrsig, F. Diederich, *Helv. Chim. Acta* **1993**, *76*, 1231.

[11] M. Saunders, R. J. Cross, H. A. Jiménez-Vázquez, R. Shimshi, A. Khong, *Science* **1996**, *271*, 1693.

[12] A. B. Smith III, R. M. Strongin, L. Brard, G. T. Furst, W. J. Romanow, K. G. Owens, R. C. King, *J. Am. Chem. Soc.* **1993**, *115*, 5829.

[13] M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, J. J. P. Stewart, *J. Am. Chem. Soc.* **1985**, *107*, 3902.

[14] J. J. P. Stewart, *J. Comput. Chem.* **1989**, *10*, 209.

[15] Y. Rubin, F. Diederich, in 'Stimulating Concepts in Chemistry', Eds. F. Vögtle, J. F. Stoddart, M. Shibasaki, Wiley-VCH, Weinheim, 2000, pp. 163–186.

[16] G. Schick, T. Jarrosson, Y. Rubin, *Angew. Chem.* **1999**, *111*, 2508; *Angew. Chem., Int. Ed.* **1999**, *38*, 2360; M. J. Arce, A. L. Viado, Y. Z. An, S. I. Khan, Y. Rubin, *J. Am. Chem. Soc.* **1996**, *118*, 3775.

[17] J. C. Hummelen, M. Prato, F. Wudl, *J. Am. Chem. Soc.* **1995**, *117*, 7003; L. L. Shiu, K. M. Chien, T. Y. Liu, T. I. Lin, G. R. Her, T. Y. Luh, *J. Chem. Soc., Chem. Commun.* **1995**, 1159; C. K. F. Shen, H. H. Yu, C.-G. Juo, K.-M. Chien, G.-R. Her, T.-Y. Luh, *Chem. Eur. J.* **1997**, *3*, 744; G. X. Dong, J. S. Li, T. H. Chan, *J. Chem. Soc., Chem. Commun.* **1995**, 1725; P. R. Birkett, A. G. Avent, A. D. Darwish, H. W. Kroto, R. Taylor, D. R. M. Walton, *J. Chem. Soc., Chem. Commun.* **1995**, 1869; G. Schick, A. Hirsch, H. Mauser, T. Clark, *Chem. Eur. J.* **1996**, *2*, 935.

[18] R. F. Haldimann, ETH Dissertation Nr. 12856, Zürich, 1998.

[19] R. C. Haddon, *J. Am. Chem. Soc.* **1990**, *112*, 3385.

[20] a) F.-G. Klärner, V. Glock, J.-L. Hemmes, *Chem. Ber.* **1990**, *123*, 1869; b) F.-G. Klärner, R. Band, V. Glock, W. A. König, *Chem. Ber.* **1992**, *125*, 197.

[21] E.-U. Wallenborn, R. F. Haldimann, F.-G. Klärner, F. Diederich, *Chem. Eur. J.* **1998**, *4*, 2258.

[22] M. Prato, Q. C. Li, F. Wudl, V. Lucchini, *J. Am. Chem. Soc.* **1993**, *115*, 1148; A. B. Smith III, H. Tokuyama, *Tetrahedron* **1996**, *52*, 5257; G. Schick, T. Grösser, A. Hirsch, *J. Chem. Soc., Chem. Commun.* **1995**, 2289; T. Grösser, M. Prato, V. Lucchini, A. Hirsch, F. Wudl, *Angew. Chem.* **1995**, *107*, 1462; *Angew. Chem., Int. Ed.* **1995**, *34*, 1343.

[23] M. Cases, M. Duran, J. Mestres, N. Martín, M. Solà, *J. Org. Chem.* **2001**, *66*, 433.

[24] M. H. Hall, H. Lu, P. B. Shevlin, *J. Am. Chem. Soc.* **2001**, *123*, 1349; see also: F. Diederich, L. Isaacs, D. Philp, *Chem. Soc. Rev.* **1994**, 243; F. Diederich, L. Isaacs, D. Philp, *J. Chem. Soc., Perkin Trans. 2* **1994**, 391.

[25] L. Isaacs, A. Wehrsig, F. Diederich, *Helv. Chim. Acta* **1993**, *76*, 1231; F. Diederich, U. Jonas, V. Gramlich, A. Herrmann, H. Ringsdorf, C. Thilgen, *Helv. Chim. Acta* **1993**, *76*, 2445.

Received March 27, 2001