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Fullerenes by Pyrolysis of Hydrocarbons and Synthesis of Isomeric Methanofullerenes

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Abstract: *In part A the pyrolysis of various hydrocarbons, cyclopentadienide metal complexes, and mellitic acid anhydride leading to fullerenes is introduced. Possible mechanisms are discussed on the background of the structures of the educt molecules.*
In part B the synthesis of some new 'crowned methanofullerenes' in a new one-step reaction is described. The influence of the substituents on the separation of the resulting isomers is investigated. Calculations were made to obtain information about the formation and isomerisation of these isomers. Copyright © 1996 Elsevier Science Ltd

Part A: Introduction

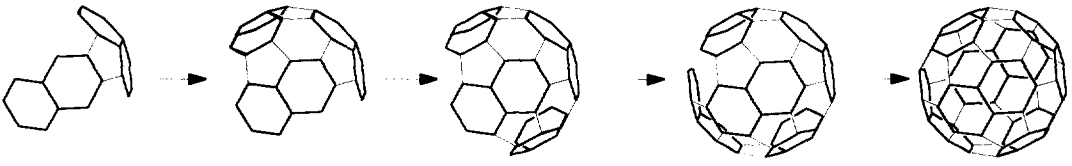
Since the discovery of the fullerenes[1] many investigations and hypotheses were published concerning the mechanism of their formation.[2-6] In the meantime it was shown that these new carbon allotropes can not only be produced from graphite but also by the pyrolysis of the hydrocarbons acetylene, 1,3-butadiene, benzene, and naphthalene.[7-19] There are many evidences that the fullerenes produced from hydrocarbons do not form by the same mechanism as fullerenes from graphite, but that large polycyclic aromatic hydrocarbons (PAH) are their precursors. By the pyrolysis of various hydrocarbons, cyclopentadienide metal complexes, and mellitic acid anhydride we tried to get more evidence for the mechanism of this kind of fullerene formation.

Hypotheses of Fullerene Formation

The formation of fullerenes from graphite was cleared up by *Bowers* et al.[6] They showed by a gas phase ion chromatography technique that the fullerenes are formed from small linear clusters (up to C_{10}) followed by planar mono-, bi-, and tricyclic rings (up to C_{60}). 'Heating' these large ring systems leads to fullerene formation accompanied by the evaporation of small carbon fragments (C_2 for even and C_1 or C_3 for odd systems). The fullerenes first appear at C_{30} and dominate at C_{50}.

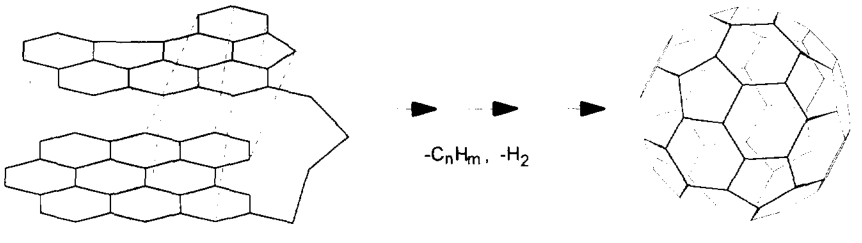
The pyrolysis of hydrocarbons came into interest because of the possibility of a continuous production method for fullerenes. *Homann* et al. and *Howard* et al. showed that fullerenes and fullerene nanotubes can be obtained from low-pressure premixed flames of acetylene, 1,3-butadiene, or benzene with oxygen.[7-13, 18, 19] *Kroto* and *Taylor* et al. produced C_{60} and C_{70} by the pyrolysis of naphthalene in an Ar-atmosphere[14-16] and *Homann* et al. showed that hydrogenated fullerenes are the direct precursors of C_{60} in a naphthalene/O_2-flame.[17]

Kroto and *Taylor* et al. proposed a mechanism of elimination of H_2 from the naphthalene molecules and an addition of the remaining naphthalene radicals.[14-16] After a stepwise assembly of six naphthalene molecules in the right order for C_{60}, further hydrogen elimination and formation of curved PAHs the cage closes to the buckminsterfullerene (scheme 1). On the other hand, this hypothesis can not explain the formation of C_{70} satisfactorily.



Scheme 1. Six naphthalene-molecules adding to each other and closing to C_{60} (schematically) as proposed by *Taylor* and *Kroto* et al.[14-16]

Homann et al. disfavoured this way of a large and arched PAH, that is formed successively with an increasing number of five-membered rings and closes itself to a cage.[12] Because of the increasing ring tension such a reaction way of arched PAHs should be slower than a planar growth with occasional formation of a five-membered ring. In addition, hydrogenated compact fractions of cages were not observed.[12] On the other hand, *Homann* et al. proposed a mechanism in which two planar or nearly planar PAHs, with about half the number of C-atoms, add to each other.[12, 18] After this, further elimination of H_2 takes place and more C-atoms of the two PAHs react with each other, whereby five- and six-membered rings are formed. When all the H-atoms and additional C-atoms are eliminated and the necessary rearrangements have taken place, C_{60} is formed (scheme 2). The authors called this internal radical chain reaction 'zipper-reaction'.

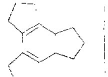
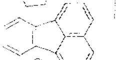
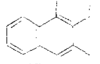
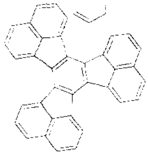
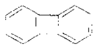
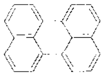
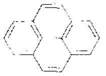
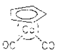
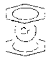
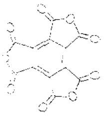


Scheme 2. Proposed mechanism by *Homann* et al.: Two large PAH adding to each other. After loss of several H_2-molecules and (if necessary) small hydrocarbons C_{60} is formed.[12]

Pyrolyses

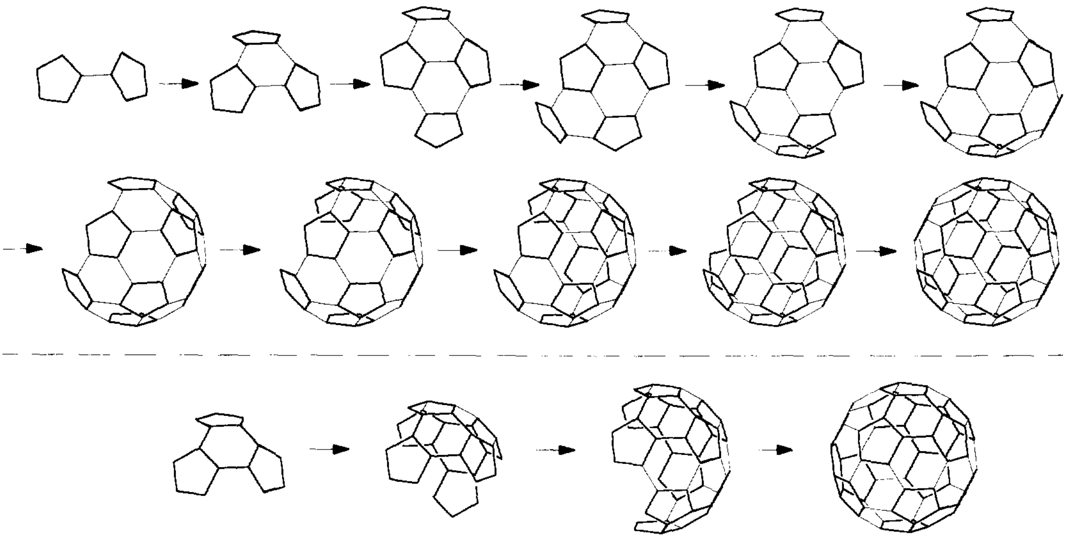
In order to prove the proposed mechanisms we pyrolysed several hydrocarbons and cyclopentadienide metal complexes under the same conditions used by *Taylor* and *Kroto* et al.[14-16] The fullerenes were isolated by column chromatography on silica gel (0.04–0.063 mm, cyclohexane/dichloromethane 10:1) and detected by TLC and HPLC.[20] In case of the detection by HPLC a mixture of the fullerene fraction of the pyrolysis and of a C_{60}-solution was used for HPLC to control that only one peak appeared. Nearly all detections were complemented by FD- or MALDI-MS. The starting compounds listed in table 1 were pyrolysed.

Table 1. Formation of C_{60} by pyrolysis of various compounds: hydrocarbons, cyclopentadienide metal complexes, mellitic acid anhydride.

Starting compound	Structure part of the C_{60}-structure?	C_{60} detected?
cyclopentadiene 	yes	yes
trindane 	yes	yes
fluoranthene 	yes	yes
triphenylene 	yes	yes
decacyclene 	yes	yes
biphenylene 	no	yes
perylene 	no	yes
pyrene 	no	yes
cyclooctatetraene 	no	no
ferrocene 	yes	yes
nickelocene 	yes	yes
cyclopentadienyl-cobalt dicarbonyl 	yes	yes
lithium cyclopentadienide 	yes	yes
bis(benzene)chromium 	yes	no
mellitic acid trianhydride 		yes

In all cases only traces of fullerenes were isolated[21] (table 1). For the hydrocarbons the best yields were obtained with cyclopentadiene.[22] Only starting with this hydrocarbon C_{60} and C_{70} could be detected by mass spectrometry in crude samples.

Apart from cyclopentadiene only trindane has a structure that directly leads to the structure of C_{60}, if the educt molecules are added to each other in the right order (scheme 3).



Scheme 3. Twelve cyclopentadiene respectively four trindane molecules adding to each other and closing to C_{60} (schematically).

In contrast, not only these two molecules with this advantage form C_{60}, but also flouranthene, triphenylene, and decacyclene. In fact, the structures of these molecules are substructures of C_{60}, but in all three cases the structures of the educt molecules can not be added to each other to lead to the structure of C_{60} without any rearrangements of the carbon skeleton.

Although the biphenylene-structure is not part of the structure of C_{60}, it is known to rearrange in a flash vacuum pyrolysis to *as*-indacene and acenaphthene,[23] which both are part of the C_{60}-structure, and C_{60} is formed, too, as we found. The structures of pyrene and perylene are not part of the C_{60}-structure, but nevertheless C_{60} is produced . Cyclooctatetraene was pyrolysed also, but no C_{60} could be detected.

Because cyclopentadiene gave the best yields of fullerenes with this method, we also used the metal complexes ferrocene, nickelocene, cyclopentadienylcobalt dicarbonyl, and lithium cyclopentadienide as pyrolyses educts. Starting with 2 g ferrocene 1.4 mg (0.1 % yield) of a fullerene fraction were produced, which is the best yield obtained with this method so far. In all three other cases C_{60} was formed, but not in visible amounts. Until now it is not clear, whether any endohedral fullerene complexes were formed or not. With bis(benzene)chromium (0) as starting material no fullerenes could be detected.

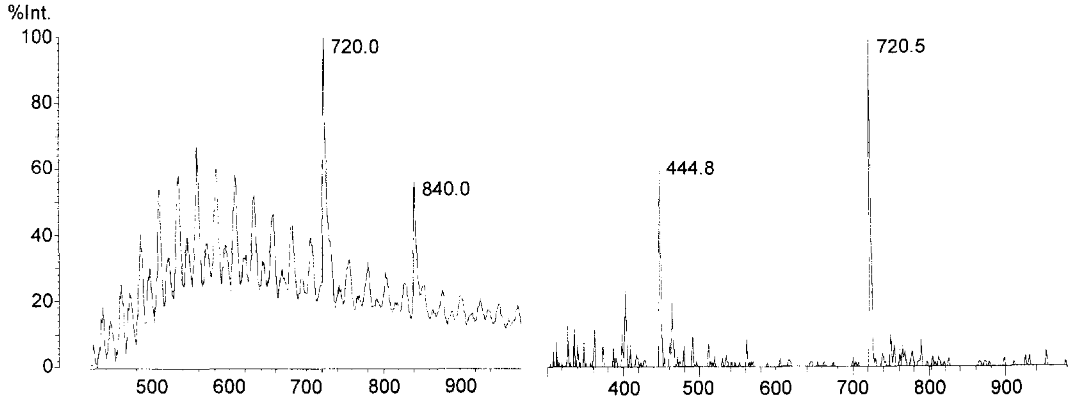


Figure 1. MALDI-TOF mass spectra of the crude pyrolysis sample of cyclopentadiene (left) and of the purified fullerene fraction of the ferrocene pyrolysis (right) showing the formation of C_{60} in both cases and the formation of C_{70} only in the case of cyclopentadiene.

In different experiments the trianhydride of mellitic acid was pyrolysed under various conditions: a) at 600 °C and 10^{-3} mbar; b) at 1000 °C in an Ar-flow of 15 ml min^{-1}; c) at 1000 °C and 140 mbar Ar-atmosphere. In all cases traces of C_{60} could be detected; the best yield (as detected by HPLC) was obtained under conditions of c) with an Ar-pressure as used in the graphite method. Surprisingly, no C_{70} could be detected.[24]

Conclusions

The fact, that cyclooctatetraene did not yield any fullerenes, seems to exclude that C_{60} is formed from any hydrocarbon. For this reason it seems not very probable that the fullerenes from hydrocarbons are formed from small (e.g. C_2) units (produced during the pyrolysis), that grow to fullerenes like in the graphite method. Also the assumption of *Taylor* and *Kroto* et al.[14-16] of six naphthalene molecules stepwise adding to each other in the right order and building up an arched PAH, that closes to a fullerene, may not be convincing. This can be concluded as not only cyclopentadiene and trindane, which are able to add to each other to the structure of C_{60} in the same way as naphthalene, yielded C_{60}, but all the other aromatic hydrocarbons used. Actually, the structures of fluoranthene, triphenylene, decacyclene, and biphenylene are substructures of C_{60} or can rearrange to one, but they can not be added to each other to the structure of C_{60}. Furthermore, even pyrene and perylene, which structures are no substructures of C_{60}, formed the buckminsterfullerene.

All these facts support the mechanism of *Homann* et al. of large PAHs adding to each other and rearranging to C_{60} after loss of several H_2-molecules.[12] On the basis of the comparatively good yields obtained with cyclopentadiene one can assume that it is advantageous, if many five-membered rings are part of the PAHs. Maybe the final rearrangements are made easier, if many five-membered rings are already present and do not have to be built up. Or due to the five-membered rings the PAHs are not absolutely planar, which makes their 'zipper-reaction' easier. But the results of the triphenylene-,[25] perylene-, and pyrene-pyrolyses clearly indicate that five-membered rings are not necessary from the start, if they can be formed during the pyrolysis. The perylene- and pyrene-pyrolyses also show that the structures of educt molecules do not have to be substructures of C_{60}-structure.

It is noteworthy that except the cyclopentadiene pyrolysis no C_{70} could be detected (which is formed in the pyrolyses of acetylene, 1,3-butadiene, benzene, and naphthalene). Maybe in these cases C_{70} is formed by one or two educt molecules adding to the two PAHs after their 'zipper-reaction' already had started. This mechanism would not be possible, if the educt molecules are too big.

The hypothesis regarding the role of the five-membered rings is underlined by the formation of C_{60} from the cyclopentadienide-metal-complexes and the best yields obtained in the pyrolyses of ferrocene. Furthermore, this is the first time that fullerenes are produced from anionic type educts. The fact, that ferrocene yields much more fullerenes than the other cyclopentadienide-metal-complexes, might indicate that this fullerene formation from anionic type educts could eventually be catalysed by the metal atoms. Again, in these cases no C_{70} could be detected.

Probably different is the C_{60}-formation from the trianhydride of mellitic acid. *Maier* et al. produced the carbon oxides C_7O_2, C_5O_2 and C_3O by flash vacuum pyrolysis of mellitic acid anhydride.[26] These carbon oxides contain linear cumulene chains. After loss of the terminal CO-groups these linear carbon-chains should add to each other and form planar rings leading to fullerenes, like the fullerene formation from graphite. But, for the time being, it is not clear why no C_{70} is formed.

Part B: Introduction

Since fullerenes are available in preparative amounts a number of different syntheses of derivatives have been reported.[27] Especially, [n+2]cycloadditions (n = 1, 2, 3, 4, 8) to the electron deficient fullerene double bonds lead to well defined products. Most of the known fullerene derivatives are synthesised via this route. Normally, the monoaddition leads to 6,6-ring bridged derivatives. Merely the formation of [2+1]cycloadducts – e. g. via [3+2]cycloaddition of diazomethanes followed by extrusion of nitrogen or addition of nitrenes – leads to more than one constitution isomer. In addition to the 'normal' 6,6-ring bridged methanofullerene, a 5,6-ring bridged isomer is formed.[28–30] At the time being, these are the only known fullerene derivatives, in which a bond in the fullerene-body is opened.

Synthesis and Characterisation

For the first time, we achieved the separation of the formed 6,6-ring (**a**) and 5,6-ring bridged (**b**) isomers with {[(benzo[15]crown-5)-4-yl]phenylmethano}[60]fullerene (**1**) using HPLC.[29] Unfortunately, it was possible to separate only small amounts of the two isomers **1a** and **1b**. This inspired us to elucidate the influence of the second substituent on the separation in order to obtain larger amounts of isomers.

Therefore, {[(benzo[15]crown-5)-4-yl]methano}[60]fullerene (**2**) bearing a small hydrogen substituent, **3** bearing a methyl group, and {bis[(benzo[15]crown-5)-4-yl]methano}[60]fullerene (**4**) bearing a rather bulky crown ether instead of the phenyl group were selected. Because the synthesis of **4** failed under the conditions used for **1**,[29] a new method for the preparation of the crowned methanofullerenes **2**, **3**, and **4** has been developed.

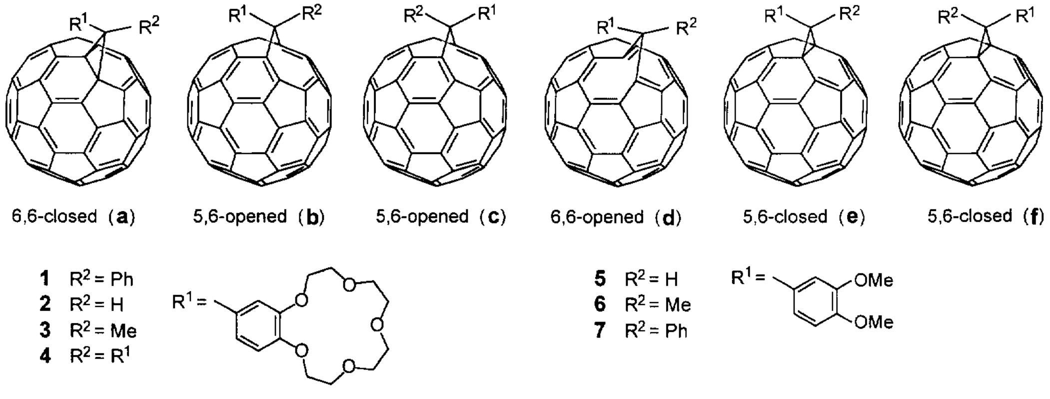
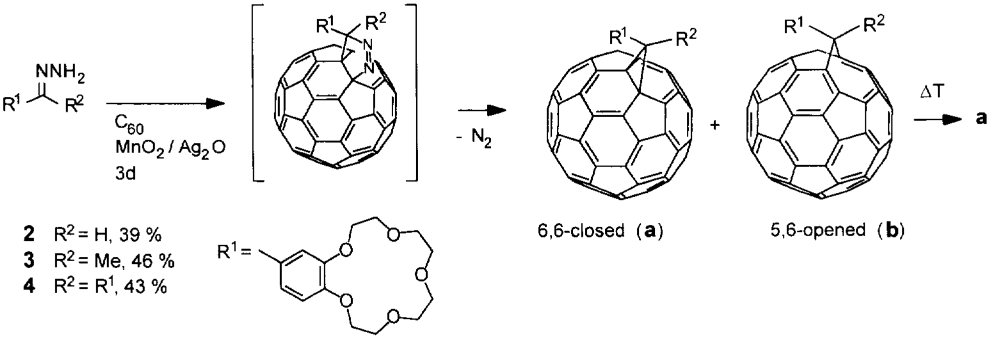


Figure 2. Possible isomers of methanofullerenes.[31]

In situ oxidation of the hydrazones by MnO_2/Ag_2O in toluene in the presence of C_{60} leads to the methanofullerenes **2**–**4** in good yields. The C_{60} is not oxidised under these conditions and the salts can be filtered easily after the reaction. No separation of the (unstable) diazomethane is necessary and the reaction can take place at room temperature to reduce side reactions. By common column chromatography on silica gel the methanofullerenes can be separated from un-reacted C_{60} and by-products and can be characterised by NMR (^1H and ^{13}C) and MS (DEI, FAB, and/or MALDI). Interestingly, in case of the unsymmetrically substituted methanofullerenes **2** and **3** only two (**a**, **b**) of the three expected (**a**, **b**, **c**) isomers are formed.[31] Until now, there is no satisfying explanation why in some cases only two (or even one)[29, 32–34] instead of three possible isomers[35] are formed.[36] The opened 5,6-ring bridged isomer **2**–**4b** can be equilibrated thermally to the isomer **2**–**4a**.



Scheme 4. Synthesis of the new methanofullerenes **2**, **3** and **4** by *in situ* formation of diazomethanes.

The separation of the isomers by HPLC on cyanoalkyl-substituted silica gel[29] of **1**–**4** show that the quality of the separation strongly depends on the second substituent R^2. In Figure 3 the difference of the retention time for the two isomers of **1**–**4** is shown. The best separation of the two isomers can be achieved with the small hydrogen substituent in **2**. On the other hand {bis[(benzo[15]crown-5)-4-yl]methano}-

[60]fullerene (**4**) with two bulky crowned aryl substituents can not be separated quantitatively under these conditions.

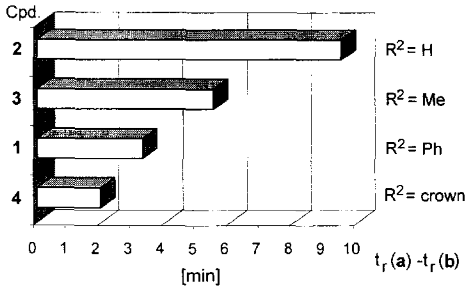


Figure 3. Comparison of the difference of the retention time of the isomers **a** and **b** in dependence of the second substituent R^2 (R^1 = crown).

This indicates that in addition to the interaction of the crown ether and the stationary phase[38] the interaction of the fullerene and the stationary phase has to be taken into account, too. The interaction of a second crown substituent ($R^2 = R^1$) with the cyanoalkyl column does not improve the separation. The volume and with that the shielding of the fullerene seems to be important so that the best separation is reached with **2** (R^2 = H).

In contrast to the other three methanofullerenes **1**, **3** and **4** (and in accordance with the results received with the HPLC) the separation of the hydrogen-substituted methanofullerene **2** to the isomers **2a** and **2b** succeeded already with normal column chromatography on silica gel with dichloromethane/methanol/aq. ammonia 400:10:1.

By NMR spectroscopy, the characterisation of the separated isomers is possible. In addition to the signals of the 16 crown methylene and the three aromatic hydrogens the ^1H NMR shows a characteristic signal of the bridgehead hydrogen H^{61}. The hydrogen of the 5,6-ring opened isomer **2b** appears at higher field than that of **2a**, by reason of the shielding area above the three double bonds (instead of two for **2a**). For the isomer **2c** a signal at lower field can be expected.[28, 29]

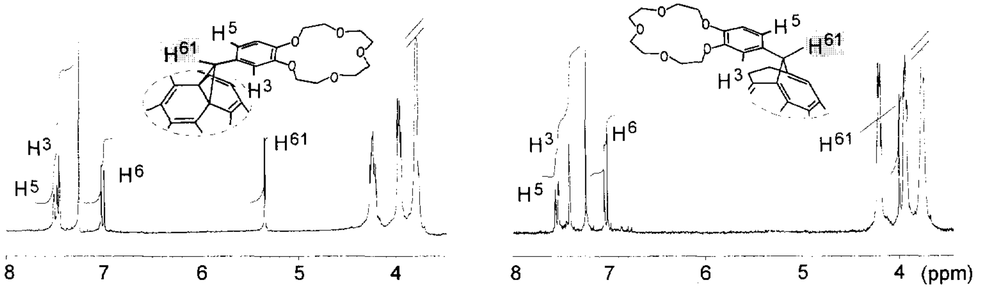


Figure 4. ^1H NMR of **2**; Isomer **2a** (left) and **2b** (right).

The ^{13}C NMR shows the expected signals for the cyclopropane subunit (C^1, C^2: 75.61 ppm; C^{61}: 43.33 ppm) and a signal for C^{62} at 125.65 ppm. The second isomer **2b** shows the signal for the bridgehead C^{61} at 53.44 ppm. The signals of the two bridged sp^2-hybridised C^1 and C^6 and of the C^{62} (because of the deshielding effect above the 'five'-ring) appear at lower field in the fullerene area and can not be assigned clearly.

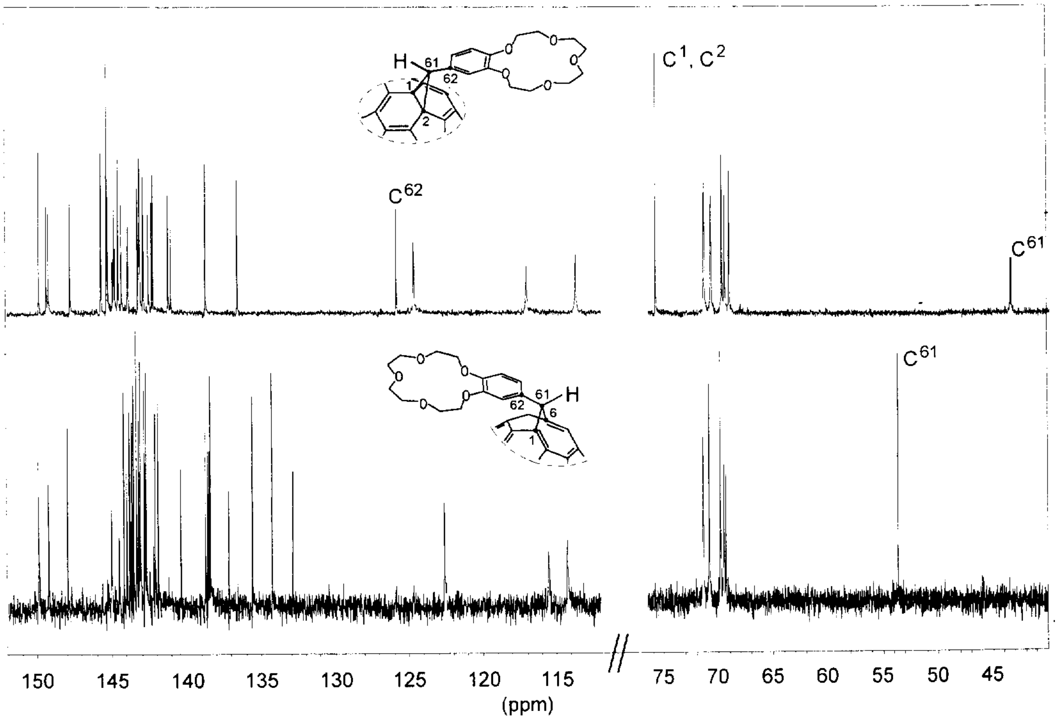


Figure 5. ^{13}C NMR of **2**; Isomer **2a** (top) showing the two signals of the cyclopropane subunit (C^1, C^2: 75.61 ppm; C^{61}: 43.33 ppm) and a signal for the C^{62} (125.65 ppm) and **2b** (bottom) showing one signal for the bridgehead C^{61} (53.44 ppm). The signals of C^1, C^6, and C^{62} are shifted to lower field and can not be assigned clearly.

Calculations

To obtain more information about the formation and equilibration of **1**–**4** semiempirical calculations with the related [(3,4-dimethoxyphenyl)methano][60]fullerene (**5**), {[(3,4-dimethoxyphenyl)methyl]methano}[60]-fullerene (**6**), and [(3,4-dimethoxyphenyl)phenyl]methano[60]fullerene (**7**) using the PM3 hamiltonian are made.[39, 40] For the relative heat of formation $\Delta H_{f,r}$[41] of the two opened 5,6-ring bridged isomers **5**–**7b** and **5**–**7c** a slight difference is observed (table 2). For the smaller substituent in **5** the difference is slightly more than in **7** but nevertheless only 1 kcal mol^{-1}. The closed 5,6-ring isomers **5**–**7e** and **5**–**7f** (that are theoretical intermediates in the formation of the opened 5,6-ring isomers) have approximately the same relative heat of formation $\Delta H_{f,r}$. Therefore, the heat of formation $\Delta H_{f,r}$ can give no satisfying explanation why **2b** respectively **3b** are formed instead of **2c** (**3c**) because the observed differences are too small. This is in accordance with results received for other methanofullerenes.[42]

In the case of the hydrogen substituted methanofullerene **5** no minima for the closed isomers **5e** and **5f** occur. This is in contrast to the mechanism for the rearrangement proposed by others[43] for the equilibration of the 5,6-ring opened isomers **b** and **c** to the thermodynamic more stable isomer **a**. In their interpretation basing

Table 2. Calculated relative heats of formation $\Delta H_{f,r}$[41] and distances d between the two bridged C-atoms.[39]

		a (6-6 closed)	**b** (5-6 opened)	**c** (5-6 opened)	**d** (6-6 opened)	**e** (5-6 closed)	**f** (5-6 closed)
$\Delta H_{f,r}$ [kcal mol^{-1}] [41]	**5**	0	2.1	3.1	*	*	*
	6	0	6.2	6.7	*	21.1	21.4
	7	0	7.4	7.5	*	21.5	21.5
$d_{C1\text{-}C2}$ ($d_{C1\text{-}C6}$) [pm]	**5**	155.5	*220.9*	*220.4*	*	*	*
	6	155.3	*219.7*	*219.7*	*	*163.0*	*162.8*
	7	155.2[#]	*219.3*	*219.1*	*	*162.2*	*162.2*

(*: no energy minimum found; #: distance obtained from X-ray diffraction $d_{C1\text{-}C2}$ = 161.4 pm[44])

on calculations with symmetrically substituted methanofullerenes the rearrangement is possible only if the 5,6-ring closed isomer is in an energy minimum on the reaction path. In accordance with the observed experimental results – that **2b** can be equilibrated to **2a** although the closed 5,6-ring isomers are not stable – a rearrangement via a biradical[33a] or an ionic intermediate[33c] and therefore the stability of the intermediates seems to be more probable. To our opinion, the ability of the substituent to stabilise the (radical or ionic) intermediates may play an important role. For example, the phenyl group can stabilise a radical or ionic intermediate better than hydrogen. This could explain, why **2b** can be equilibrated to the isomer **2a** but the hydrocarbon $C_{61}H_2$ can not.[43, 45, 28] To clear up the equilibration further calculations and investigations seem to be necessary.

Experimental Section

Part A, General Procedure: The pyrolyses were carried out under similar conditions to those used by *Taylor* and *Kroto* et al.[14-16] Amounts of 0.5 up to 5 g[46] of the starting compounds were sublimed into a silica tube (declined ca. 30°; diameter 2 cm, length 75 cm). This was heated to about 1000 °C by an oven (length 65 cm) instead of a propane/oxygen torch as used by *Taylor* and *Kroto* et al. (thus extending the heated zone) and an Ar-flow of 15 ml min^{-1} was passed through. The outlet led to a series of toluene bubblers. The toluene was black-coloured after the pyrolyses. The remainders of the pyrolyses were extracted with refluxing toluene (using the toluene of the bubblers) in order to remove the soot from the PAHs and the fullerenes.[47] The fullerenes were isolated by column chromatography on silica gel (0.04–0.063 mm, cyclohexane/dichloromethane 10:1).

Part B, General Procedure: 0.28 mmol (200 mg) C_{60} and 0.28 mmol of the corresponding hydrazone[42] are suspended in 250 ml toluene in an ultrasonic bath, 500 mg manganese dioxide and 20 mg silver oxide are added and the suspension is stirred vigorously for three days. The suspension is filtered, the solvent is removed and the crude product is chromatographed over a short silica gel column (solvent gradient: toluene → dichloromethane/methanol 20:1) to separate from unreacted C_{60}. The crude product is chromatographed over silica gel (dichloromethane/methanol/aq. ammonia 400:10:1).

The isomeric mixture of the methanofullerenes is equilibrated to the thermodynamic most stable isomer **a** by dissolving in 200 ml toluene and stirring for three days at 105 °C.

HPLC separation:[29] Column: LiChrosorb CN 5 μm, 250 × 8 mm; solvent: trichloromethane/*n*-hexane 9:1; flow: 1.0 ml min^{-1}; pressure: 30 bar; detection: UV, $\lambda = 300$ nm.
retention times: t_r(**1a**) = 19.5 min, t_r(**1b**) = 22.8 min; t_r(**2a**) = 17.5 min, t_r(**2b**) = 27.0 min; t_r(**3a**) = 17.5 min, t_r(**3b**) = 22.5 min; t_r(**4a**) = 22.9 min, t_r(**4b**) = 24.9 min.

{[(Benzo[15]crown-5)-4-yl]methylmethano}[60]fullerene **3a** (isomer with methanonaphthalene-structure):

$C_{76}H_{22}O_5$. - 130 mg (46 %). - $R_f = 0.22$ ($CHCl_3/CH_3OH/NH_3$ (aq) 200:10:1). - mp.: > 250 °C. - MS (DEI): *m/z* (%) = 1014.0 (10) $[M^+]$, 881.9 (5) $[M^+\text{-}3C_2H_4O]$, 720.0 (100) $[M^+\text{-}C_{16}H_{22}O_5]$. - MS (FAB): *m/z* (%) = 1038.2 (4) $[M+Na^+]$, 1014.2 (10) $[M^+]$, 720.0 (100) $[M^+\text{-}C_{16}H_{22}O_5]$. - MS (MALDI): *m/z* (%) = 1015.1 (100) $[M^-]$, 719.9 (90) $[M^-\text{-}C_{16}H_{22}O_5]$. - ^1H NMR, (250 MHz, $CDCl_3$), δ = 2.51 (s, 3 H, CH_3), 3.76 (s, 8 H, CH_2), 3.93 (m, 4 H, CH_2), 4.21 (m, 4 H, CH_2), 6.97 [d, $^3J_{HH}$ = 8.2 Hz, 1 H, ArH (6)], 7.40 [d, $^4J_{HH}$ = 1.5 Hz, 1 H, ArH (3)], 7.44 [dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.5 Hz, 1 H, ArH (5)]. - ^{13}C NMR, (62.9 MHz, $CDCl_3$), δ = 22.62 (s, 1 C, CH_3), 47.33 [s, 1 C, quart. bridge-C, C(61)], 68.78 (s, 1 C, CH_2), 69.28 (s, 1 C, CH_2), 69.56 (s, 2 C, CH_2), 70.50 (s, 1 C, CH_2), 70.56 (s, 1 C, CH_2), 71.04 (s, 1 C, CH_2), 71.09 (s, 1 C, CH_2), 81.06 [s, 2 C, quart. bridged C, C(1), C(2)], 113.36 (s, 1 C, CH), 116.69 (s, 1 C, CH), 124.23 (s, 1 C, CH), 131.98 [s, 1 C, C(62)], 137.69, 137.92, 140.68, 140.85, 142.06, 142.16, 142.21, 142.85, 142.91, 142.99, 143.66, 143.89, 144.26, 144.34, 144.55, 144.70, 144.91, 144.95, 145.01, 145.07, 145.81, 148.02, 148.73, 148.79 (s, quart. C).

{Bis[(benzo[15]crown-5)-4-yl]methano}[60]fullerene **4a** (isomer with methanonaphthalene-structure):

$C_{89}H_{38}O_{10}$. -151 mg (43 %). - $R_f = 0.15$ ($CHCl_3/CH_3OH/NH_3$ (aq) 200:10:1). - mp.: > 250 °C. - MS (DEI), *m/z* (%) = 1266.4 (2) $[M^+]$, 1222.3 (<1) $[M^+\text{-}C_2H_4O]$, 1178.3 (<1) $[M^+\text{-}2C_2H_4O]$, 1134.3 (1) $[M^+\text{-}3C_2H_4O]$, 1002.2 (2) $[M^+\text{-}6C_2H_4O]$, 720.0 (100) $[M^+\text{-}C_{29}H_{38}O_{10}]$. - MS (MALDI): *m/z* (%) = 1267.7 (45) $[M^-]$, 720.5 (100) $[M^-\text{-}C_{29}H_{38}O_{10}]$. - ^1H NMR, (250 MHz, $CDCl_3$), δ = 3.76 (s, 16 H, CH_2), 3.93 (m, 8 H, CH_2), 4.20 (m, 8 H, CH_2), 6.94 [d, $^3J_{HH}$ = 8.2 Hz, 2 H, ArH (6)], 7.52 [d, $^4J_{HH}$ = 2.1 Hz, 2 H, ArH (3)], 7.60 [dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 2.1 Hz, 2 H, ArH (5)]. - ^{13}C NMR, (62.9 MHz, $CDCl_3$), δ = 57.71 [s, 1 C, quart. bridge-C, C(61)], 68.83 (s, 4 C, CH_2), 69.65 (s, 4 C, CH_2), 70.53 (s, 2 C, CH_2), 70.66 (s, 2 C, CH_2), 71.09 (s, 2 C, CH_2), 71.17 (s, 2 C, CH_2), 79.47 [s, 2 C, quart. bridged C, C(1), C(2)], 113.60 (s, 2 C, CH), 117.30 (s, 2 C, CH), 124.37 (s, 2 C, CH), 132.08 [s, 2 C, C(62), C(68)], 138.33, 140.79, 142.13, 142.34, 142.89, 143.05, 143.86, 144.26, 144.64, 144.72, 145.13, 145.18, 145.27, 145.64, 148.34, 148.80, 149.09 (s, quart. C).

{[(Benzo[15]crown-5)-4-yl]methano}[60]fullerene **2a** (isomer with methanonaphthalene-structure):

yield **2a** + **2b**: 108 mg (39 %)
$C_{75}H_{20}O_5$. - 59 mg (21 %). - $R_f = 0.27$ ($CHCl_3/CH_3OH/NH_3$ (aq) 200:10:1). - mp.: > 250 °C. - MS (DEI), *m/z* (%) = 1000.1 (<1) $[M^+]$, 868.1 (1) $[M^+\text{-}3C_2H_4O]$, 720.0 (100) $[M^+\text{-}C_{15}H_{20}O_5]$. - MS (MALDI): *m/z* (%) = 1001.0 (100) $[M^-]$. - ^1H NMR, (250 MHz, $CDCl_3$), δ = 3.79 (s, 8 H, CH_2), 3.96 (m, 4 H, CH_2), 4.23 (m, 4 H, CH_2), 5.35 (s, 1 H, CH), 7.01 [d, $^3J_{HH}$ = 8.2 Hz, 1 H, ArH (6)], 7.45 [d, $^4J_{HH}$ = 2.0 Hz, 1 H, ArH (3)], 7.49 [dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 2.0 Hz, 1 H, ArH (5)]. - ^{13}C NMR, (62.9 MHz, $CDCl_3/CS_2$), δ = 43.33 [s, 1 C, bridge-CH, C(61)], 68.91 (s, 1 C, CH_2), 69.31 (s, 1 C, CH_2), 69.58 (s, 2 C, CH_2) 70.55 (s, 1 C, CH_2), 70.60 (s, 1 C, CH_2), 71.16 (s, 1 C, CH_2), 71.20 (s, 1 C, CH_2), 75.61 [s, 2 C, quart. bridged C, C(1), C(2)], 113.54 (s, 1 C, CH), 116.66 (s, 1 C, CH), 124.49 (s, 1 C, CH), 125.65 [s, 1 C, C(62)], 136.36 (s, 2 C, quart. C), 138.50 (s, 2 C, quart. C), 140.78 (s, 2 C, quart. C), 140.97 (s, 2 C, quart. C), 141.99 (s, 2 C, quart. C), 142.07 (s, 2 C,

quart. C), 142.29 (s, 2 C, quart. C), 142.63 (s, 2 C, quart. C), 142.84 (s, 2 C, quart. C), 142.87 (s, 4 C, quart. C), 142.99 (s, 2 C, quart. C), 143.64 (s, 4 C, quart. C), 144.09 (s, 2 C, quart. C), 144.30 (s, 2 C, quart. C), 144.32 (s, 2 C, quart. C), 144.51 (s, 1 C, quart. $COCH_2$), 144.58 (s, 2 C, quart. C), 144.61 (s, 2 C, quart. C), 144.69 (s, 1 C, quart. $COCH_2$), 144.98 (s, 2 C, quart. C), 145.04 (s, 4 C, quart. C), 145.09 (s, 2 C, quart. C), 145.44 (s, 4 C, quart. C), 147.52 (s, 2 C, quart. C), 148.99 (s, 2 C, quart. C), 149.13 (s, 2 C, quart. C), 149.63 (s, 2 C, quart. C).

{[(Benzo[15]crown-5)-4-yl]methano}[60]fullerene **2b** (isomer with methanocyclononatetraene-structure):

$C_{75}H_{20}O_5$. - 49 mg (18 %). - R_f = 0.26 ($CHCl_3/CH_3OH/NH_3$ (aq) 200:10:1). - mp.: > 250 °C. - MS (DEI), *m/z* (%) = 1000.1 (<1) [M^+], 868.0 (1) [M^+-$3C_2H_4O$], 719.9 (100) [M^+-$C_{15}H_{20}O_5$]. - MS (MALDI): *m/z* (%) = 1001.0 (100) [M^-]. - ^{1}H NMR, (250 MHz, $CDCl_3$), δ = 3.78 (s, 8 H, CH_2), 3.96 (m, 4 H, CH_2), 4.02 (s, 1 H, CH), 4.23 (m, 4 H, CH_2), 7.05 [d, $^3J_{HH}$ = 8.3 Hz, 1 H, ArH (6)], 7.42 [d, $^4J_{HH}$ = 2.1 Hz, 1 H, ArH (3)], 7.55 [dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 2.1 Hz, 1 H, ArH (5)]. - ^{13}C NMR, (62.9 MHz, $CDCl_3/CS_2$), δ = 53.44 [s, 1 C, bridge-CH, C(61)], 69.12 (s, 1 C, CH_2), 69.30 (s, 1 C, CH_2), 69.62 (s, 2 C, CH_2), 70.62 (s, 2 C, CH_2), 71.19 (s, 2 C, CH_2), 114.08 (s, 1 C, CH), 115.34 (s, 1 C, CH), 122.41 (s, 1 C, CH), 132.68, 134.07, 135.40, 136.98, 138.20, 138.30, 138.39, 138.54, 140.19, 141.70, 141.91, 142.00, 142.49, 142.58, 142.62, 142.88, 143.00, 143.11, 143.15, 143.35, 143.47, 143.55, 143.61, 143.78, 143.82, 144.00, 144.29, 144.79, 144.84, 147.75, 149.05, 149.74 (s, quart. C).

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21. Invisible amounts, if not indicated otherwise. In a benzene/oxygen-flame *Howard* et al. obtained optimal yields of 0.3 %.[9] The yields of hydrocarbon pyrolyses in a pure Ar-atmosphere seem to be much lower.
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46. It is not possible to use larger amounts, since a silica tube with this diameter would be blocked then.

47. *Kroto* and *Taylor* et al. first removed the acetone-soluble hydrocarbons, as fullerenes are nearly insoluble in acetone. But during our investigations we realised that in such low concentrations parts of the fullerenes are soluble in acetone: therefore we did not remove the acetone-soluble part.

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