152. Chemistry of the Higher Fullerenes: Preparative Isolation of C_{76} by HPLC and Synthesis, Separation, and Characterization of *Diels-Alder* Monoadducts of C_{70} and C_{76}

by **Andreas Herrmann, François Diederich***, and **Carlo Thilgen**

Laboratorium für Organische Chemie, ETH-Zentrum, Universitätstrasse 16, CH-8092 Zürich

and **Hans-Ulrich ter Meer** and **Wolfgang H. Müller**

Hoechst AG, Angewandte Physik – G864, D-65926 Frankfurt am Main

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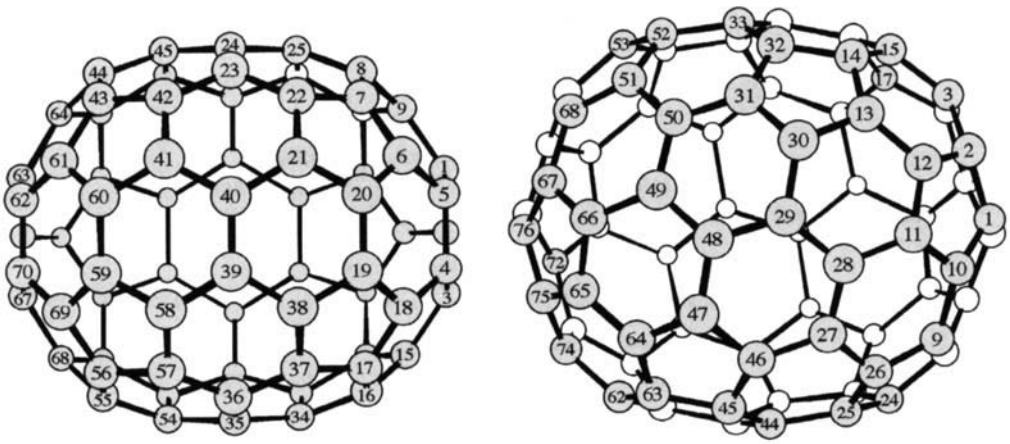
HPLC Separation of higher fullerenes was compared on two different stationary phases, and the preparative isolation of pure C_{76} is described. Higher-fullerene derivatives **1** and **2** were prepared by *Diels-Alder* reaction of C_{70} and C_{76} with an *ortho*-quinodimethane intermediate generated *in situ*. Three out of four possible isomeric C_{70} monoadducts, *i.e.* **1a–c**, and, for the first time, one isomeric C_{76} monoadduct, *i.e.* **2c**, could be isolated in pure form and characterized by ^{1}H-NMR, ^{13}C-NMR, UV/VIS, and mass spectrometry. Five other C_{76} isomers *i.e.*, **2a,b,d–f** were obtained in partially separated product fractions. Coalescence temperatures and energy barriers were determined for the cyclohexene-ring inversion in two of the isomeric C_{70} derivatives. The structure of the C_{70} adducts could be deduced unambiguously from symmetry considerations based on high- and low-temperature ^{1}H-NMR spectroscopy. A simple model for the qualitative evaluation of the local curvature of fullerene surfaces is presented and used for the prediction of addition sites in higher fullerenes. These predictions are compared to the experimental results mentioned above as well as to predictions resulting from π-bond-order considerations and from calculated pyramidalization angles.

1. Introduction. – The availability of gram quantities of pure C_{60} by simple chromatographic methods [1] led to numerous investigations on the chemical properties of buckminsterfullerene [2]. Compared to I_h-C_{60}, the lower symmetry of the known higher fullerenes leads to the formation of a large number of possible structural isomers which are difficult to separate in most cases. Some experimental as well as theoretical efforts have been undertaken to investigate the regioselectivity of addition reactions to C_{70} [3–9]. A single reaction of C_{76} to generate derivatives has been described so far, but none of the addition products was characterized [10].

The initial goal of this work was the isolation of pure C_{70} and C_{76} (*Fig. 1*) in quantities sufficient for subsequent chemical transformations. Whereas the purification of C_{70}, in analogy to that of C_{60}, can be achieved by gravity column chromatography [1a, b], the separation of the larger carbon spheres requires more elaborate methods, and only very small quantities only can be processed in general. High-performance liquid chromatography (HPLC) proved to be a powerful tool for the separation of higher fullerenes as well as of fullerene adducts, and a large number of stationary phases and eluents have been tested for this purpose [11]. Following the initial successful use of reversed-phase silica gel [11b–g], π-acidic phases were reported to give a particularly good separation of the larger carbon spheres [10] [11k, l]. To achieve a convenient preparative separation of the higher



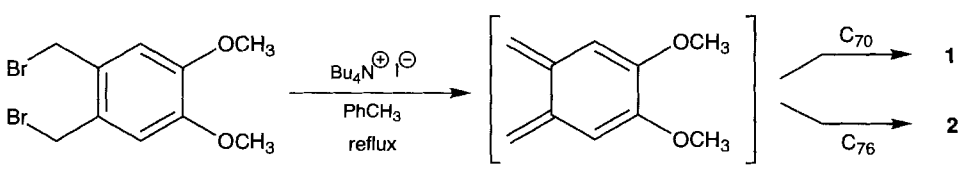
D_{5h}-C_{70} D_2-C_{76}

Fig. 1. *Structures of* D_{5h}-C_{70} *and* D_2-C_{76}. Numbering of C-atoms according to [9a].

fullerenes, the performance of different stationary phases was compared in this study, and the operating conditions were optimized.

The central theme in this paper is the regioselectivity of the functionalization of C_{70} and C_{76} by *Diels-Alder* reaction with an *o*-quinodimethane derivative generated *in situ* (*Scheme*). A number of [4 + 2] cycloadditions of this type were reported for C_{60} [12] [13].

Scheme. *Synthesis of* Diels-Alder *Adducts* **1** *and* **2**



Besides NMR-spectroscopic evidence, X-ray crystal structures of different adducts have clearly shown that the *Diels-Alder* reaction occurred selectively at the junction between two six-membered rings ([6,6] bond) [12b, c] [13]. The fact that no adducts from attack at [6,5] bonds (bonds at the junction between a six- and a five-membered ring) are to be expected considerably simplifies the product distribution, particularly in the case of the higher fullerenes. In addition, *o*-quinodimethane addition leads to the formation of an aromatic ring system, thus stabilizing the reaction product [12] [13].

Here we report the synthesis of derivatives of C_{70} and C_{76} by *Diels-Alder* reaction under conditions similar to those previously applied to the corresponding reaction with C_{60} [12b]. HPLC Separation of product mixture **1** gave three pure regioisomeric C_{70} adducts, **1a–c** which could be fully characterized. In the case of C_{76}, one isomerically pure monoadduct, **2c**, could be isolated and characterized for the first time; five other isomers, **2a, b, d–f**, were obtained in partially separated product mixtures. Also, a simple model for the prediction of addition sites in higher fullerenes is presented.

2. Results and Discussion. – 2.1. *The Isomeric Distribution of Higher-Fullerene Adducts.* In the case of I_h-C_{60}, all C-atoms are identical, and addition can occur at two different bonds, a [6,6] and a [6,5] bond, only. D_{5h}-C_{70} exhibits five different types of C-atoms, and eight different bonds can be distinguished, four of which are [6,6] bonds [5a,c]. Chiral D_2-C_{76} consists of 19 different C-atoms (four of each type) and 30 different bonds; half of them are [6,6] and the other half [6,5] bonds [11c].

In most reactions with C_{60}, addition occurred at the shorter [6,6] bonds with a higher double-bond character, rather than at the longer [6,5] bonds [2], thus leading to the formation of only one single monoadduct. For C_{70}, theoretical studies predicted the regioselective addition to the [6,6] bonds of the polar caps, and this functionalization pattern has been found in several experimental investigations [3–9].

Semi-empirical MOPAC/AM1 [3a] and MNDO [4a] calculations have been carried out for hydrogen or nucleophile adducts of C_{70}. In the case of $C_{70}H_2$ and $C_{70}MeH$, both methods predicted the 7,8-isomer to be the most stable, followed by the 1,9-isomer. *Ab initio* calculations at the *Hartree-Fock* level using 3-21G and 6-31G* basis sets, however, inverted the stability order of these two isomers [4a]. On the other hand, 1,4-addition was predicted to take place preferentially at the equator of C_{70} [3a] [4a].

Experimental investigations have shown that addition of nucleophiles [3b,c] as well as hydrogenation [4b,c] or the formation of metal complexes [5] were regioselective and led preferentially to the 1,9-isomer of C_{70}, besides some 7,8-adduct, in most cases. Addition of OsO_4 to C_{70} thus gave the two isomers in a ratio of 2.1:1 [5c]. By equilibrating the mixture of 1,9- and 7,8-isomers of $C_{70}H_2$, *Cahill* and coworkers have shown that the former is thermodynamically favored over the latter by 1.4 kcal/mol [4c]. This result is in good agreement with the *ab initio* calculations [4a]. Also, multiple hydrogenation was found to occur mainly at the poles of the molecule [4d, e]. *Ando* and coworkers recently prepared the first C_{70} adduct, in which reaction occurred at the equatorial belt (23,24-isomer), by photochemical cycloaddition of a disilirane [6]. *Smith* reported the reaction of C_{70} with diazomethane leading to the formation of several $C_{71}H_2$ isomers bridged at [6,6] or at [6,5] ring junctions [7]. Investigations on the regiochemistry of radical additions were based on electron spin resonance studies [7b]. *Diels-Alder* reactions of C_{70} with 1,3-cyclopentadiene were studied in solution [8a] and in the gas phase [8b]. *Kroto, Taylor*, and coworkers reported the reaction of C_{70} with pentamethylcyclopentadiene to take place mainly at the 1,9 position of the fullerene [8c]. Due to the fact that none of the isomers described was obtained in pure form, the assumption of a 7,8-isomer also being formed could not be proved unambiguously [8c].

Several approaches have been taken to allow more general predictions of the most reactive sites in higher fullerenes. Based on the assumption that addition should occur preferentially at the bonds with the highest π-bond order, π-electron densities have been calculated by *Taylor* using the *Hückel* MO method [9a]. In the case of C_{70}, however, the above-mentioned experimental results [3–5] [7] [8], showing that addition takes place preferentially at the C(1)–C(9) bond (which is assigned a lower π-bond order compared to the C(7)–C(8) bond), are not in agreement with the prediction.

A different approach to a classification of fullerene bond reactivities takes account of the local curvature of the carbon spheres, with the strongest curvature corresponding to the most reactive bond. To express the local curvature at different sites of a π-system, *Haddon* and coworkers calculated pyramidalization angles of different C-atoms by ap-

plying the concept of the π-orbital axis vector (POAV) to fullerenes [14]. The values reported in [5c] [10] [14], which take rehybridization as the change in electronic structure due to deformation and other parameters into account, show that the greatest local curvature occurs at pyracylene-type bonds, *i.e.*, [6,6] bonds with each C-atom also belonging to a pentagon.

2.2. *Qualitative Model for the Evaluation of Bond Reactivities in Fullerenes.* To have a qualitative tool for the prediction of addition sites, we developed a simple model for the evaluation of the curvature of fullerene bonds. The curvature of a fullerene surface is caused by the insertion of 12 pentagons (bond angles *ca.* 108°) into a network of hexagons (bond angles *ca.* 120°). A [6,6] bond on the fullerene surface can be assumed to be the more curved and, therefore, the more reactive, the more pentagons are located close to it.

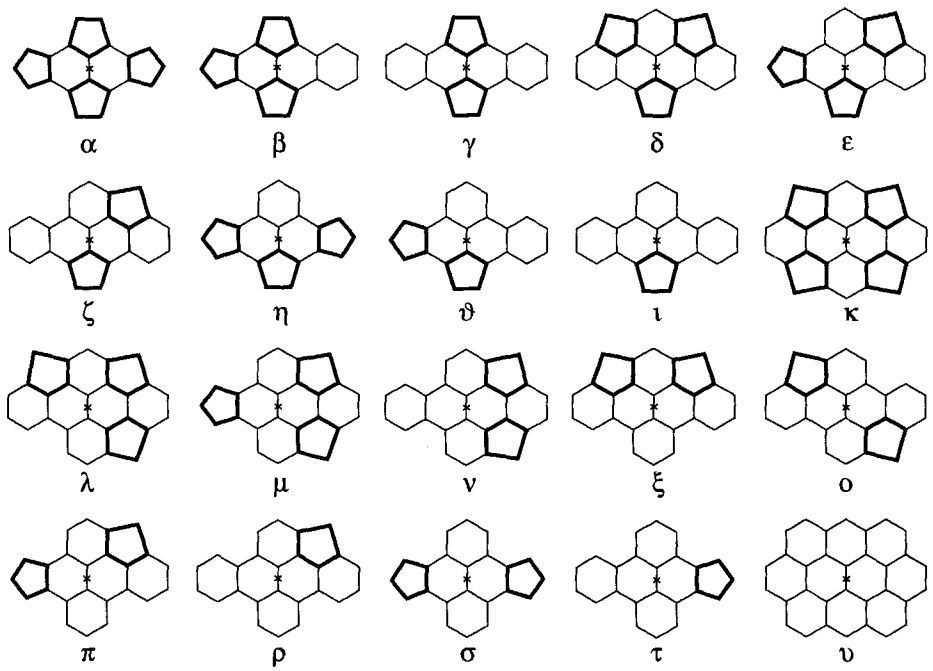


Fig. 2. *Curvature of a given bond* ('×') *as a function of its local environment: 20 possible IPR* ('isolated-pentagon rule') *satisfying arrangements of pentagons around a central naphthalene unit.* The structures are ordered according to *1*) the maximum number of pentagons in position 'a' followed by 'b' and 'c' (see *Table 1*) and *2*) the total number of pentagons in the whole structural subunit.

If one looks at a [6,6] bond of a fullerene as the central bond of a naphthalene subunit and, under observation of the isolated pentagon rule [11f], considers the rings condensed to this unit, there exist a total of 20 possible arrangements containing up to four pentagons (*Fig. 2*). The location and number of five-membered rings in this local environment of a [6,6] bond should have a determining influence on its curvature, and hence on its reactivity.

Table 1 gives a survey on the different local environments of a [6,6] bond (marked by '×') that are found in fullerenes C_{60}, C_{70}, C_{76}, C_{2v}-C_{78}, and D_3-C_{78}. Depending on whether

pentagons are separated from the bond in question by zero, one, or two bonds, their position is designated by 'a', 'b', or 'c', respectively, and the number of pentagons in each position is indicated (see *Table 1*). The closer a pentagon is located to the C-atoms of bond '×', the stronger is its pyramidalizing effect. Maximum curvature is observed for five-membered rings in position 'a' which share two edges with the central naphthalene unit. Two pentagons of this type lead to the formation of a pyracylene (= cyclo-

Table 1. *Classification of [6,6] Bonds ('×') According to Their Local Environment and Their Occurrence in Different Fullerenes*

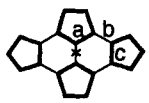
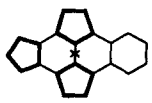
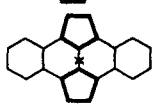
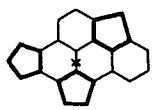
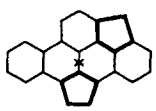
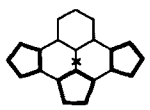
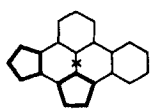
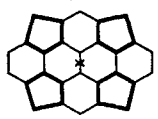
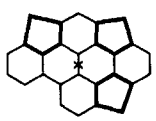
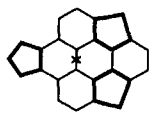
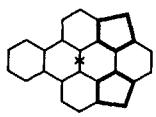
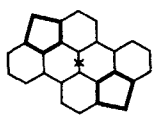
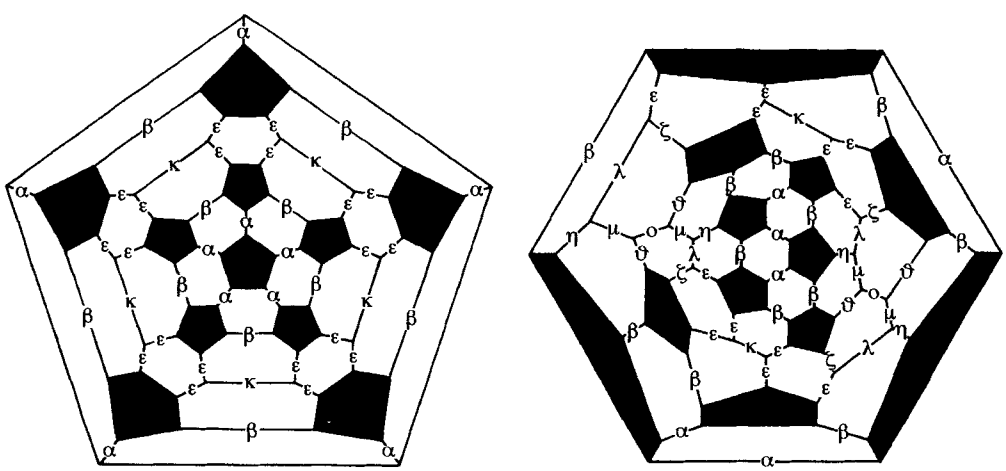
Bond type	Local environment	Number of pentagons[a])			Number of bonds[b])				
		a	b	c	I_h-C_{60}	D_{5h}-C_{70}	D_2-C_{76}	C_{2v}-C_{78}	D_3-C_{78}
α		2	0	2	30	10	6	4	6
β		2	0	1	–	10	12	10	12
γ		2	0	0	–	–	–	3	–
ε		1	1	1	–	20	12	12	6
ζ		1	1	0	–	–	4	4	6
η		1	0	2	–	–	4	10	6
ϑ		1	0	1	–	–	4	–	6
κ		0	4	0	–	5	2	2	–
λ		0	3	0	–	–	4	4	6

Table 1 (cont.)

Bond type	Local environment	Number of pentagons[a])			Number of bonds[b])				
		a	b	c	I_h-C_{60}	D_{5h}-C_{70}	D_2-C_{76}	C_{2v}-C_{78}	D_3-C_{78}
μ		0	2	1	–	–	4	2	6
ν		0	2	0	–	–	–	6	–
o		0	2	0	–	–	2	–	3
Max. number of isomers[c]) resulting from monoaddition to bond types α and β				1	2	5	4	3	

[a]) Number of pentagons in positions 'a', 'b', and 'c'.
[b]) Number of [6,6] bonds of the given type occurring in the various fullerenes.
[c]) It should be noted that reactions taking place at the same type of bonds (same *local* environment) do not necessarily lead to identical addition products.

pent[*fg*]acenaphthylene) substructure. Besides the position of the pentagons, their number is also relevant in determining the local curvature. The most curved bonds and, therefore, the most reactive ones are those of type α and β which are embedded in a pyracylene substructure with additional five-membered rings in position 'c'. The distribution of the different bond types on the surface of C_{70} and C_{76} is shown in the corresponding



D_{5h}-C_{70} D_2-C_{76}

Fig. 3. Schlegel *diagrams of* C_{70} *and* C_{76} *showing the distribution of different types of [6,6] bonds with a given local curvature* (*cf. Table 1*)

Schlegel diagrams (*Fig. 3*). According to this description, the most reactive C(1)–C(9) bond in C_{70} is of type α and the less reactive C(7)–C(8) bond of type β.

2.3. *High-Performance Liquid Chromatography* (HPLC). The investigation of the chemical properties of higher fullerenes necessitates mg quantities of pure allotropes. HPLC has proved to be a powerful tool for the separation and purification of higher fullerenes [10] [11]. Very good separation methods have been elaborated for reversed-phase silica gel as the stationary phase [11b–g]. The main disadvantage of this phase is the fact that only very small quantities of material can be processed since the fullerenes are only scarcely soluble in the solvent mixture used as eluent. π-Acidic phases like tetrachlorophthalimidopropyl-modified silica gel (TCPP) [11l] gave an excellent separation and could be more heavily loaded, but this stationary phase is not readily available in the larger quantities needed for preparative-scale work.

To work out the best conditions for a preparative separation of higher fullerenes, the performances of two commercial nitroaromatic π-acceptor phases, a *Shandon Hypersil CTA* and a *Regis Buckyclutcher I* column (tris(2,4-dinitrophenoxy)alkyl-modified silica gel) [11k], were compared. The separation of higher fullerenes as well as of different addition products on a *Buckyclutcher I* column with toluene/hexane mixtures was previously reported [4c] [10] [15], but a further improvement of the ratio of separated amounts of pure fullerenes *vs.* separation time was attempted.

In the comparative studies, equal amounts of a solution of soot extract enriched in higher fullerenes (for composition, see *Exper. Part*) were injected onto both columns. Binary solvent mixtures with toluene, CH_2Cl_2, hexane, and MeCN in different ratios were used as the eluents. The best separation could be obtained on both columns with the mixtures hexane/toluene and hexane/CH_2Cl_2. A higher percentage of hexane gave a better separation in general, but the retention time increased considerably. Toluene/hexane 3:7 gave a good separation of fullerenes on the analytical *Buckyclutcher I* column (flow rate 1 ml/min, total elution time *ca.* 30 min). On the *Hypersil CTA* column, an acceptable separation was obtained with toluene/hexane 2:8 (flow rate 1 ml/min, total elution time *ca.* 13 min). Even though baseline separation was obtained for C_{60}, C_{70}, and C_{84} on both columns, the separation of C_{76} from C_{78} was less good on the *Hypersil CTA* compared to the *Buckyclutcher I* column. Similar results were obtained with binary mixtures of CH_2Cl_2 and hexane, but the lower solubility of fullerenes in these solvents constitutes a considerable disadvantage for prep. HPLC. Mixtures of toluene und MeCN, on the other hand, led to a large tailing of the peaks of C_{76}, C_{78}, and especially C_{84}.

As a conclusion, the preparative separation of higher fullerenes (*ca.* 0.7 mg per injection) was performed on a *Buckyclutcher I* column with toluene/hexane 2:3 which appeared as the best compromise between separation and retention time. Whereas baseline separation was observed for C_{60}, C_{70}, and C_{84}, two separation runs yielded C_{76} in a purity of *ca.* 97%.

2.4. Diels-Alder *Reactions*. 2.4.1. *General.* For functionalization, C_{70} or C_{76} was reacted with an excess (1.5 equiv.) of 1,2-bis(bromomethyl)-4,5-dimethoxybenzene in the presence of $(Bu_4N)I$ in refluxing toluene (*Scheme*). Column chromatography (silica gel, toluene/hexane 3:1) of the reaction mixture allowed to separate the monoadducts from higher adducts and unreacted fullerene. The separation of the monoadduct isomers was subsequently achieved by repetitive HPLC on a prep. *Buckyclutcher I* column with CH_2Cl_2/hexane 3:2. This procedure allowed a complete separation of the three C_{70}

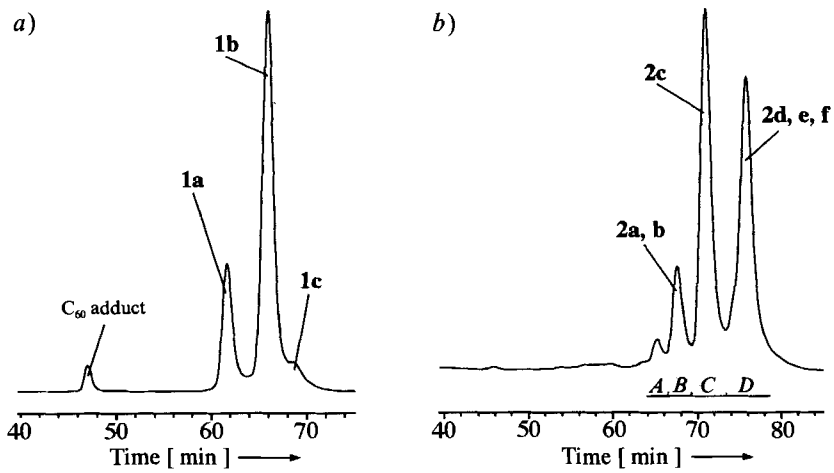


Fig. 4. *Prep. HPLC separation of* a) C_{70} *monoadducts* **1** *and* b) C_{76} *monoadducts* **2**, *with the isomeric composition being shown for each peak*. Conditions: *Buckyclutcher I* (*Regis*), CH_2Cl_2/hexane 3:2, 8 ml/min, λ = 310 nm.

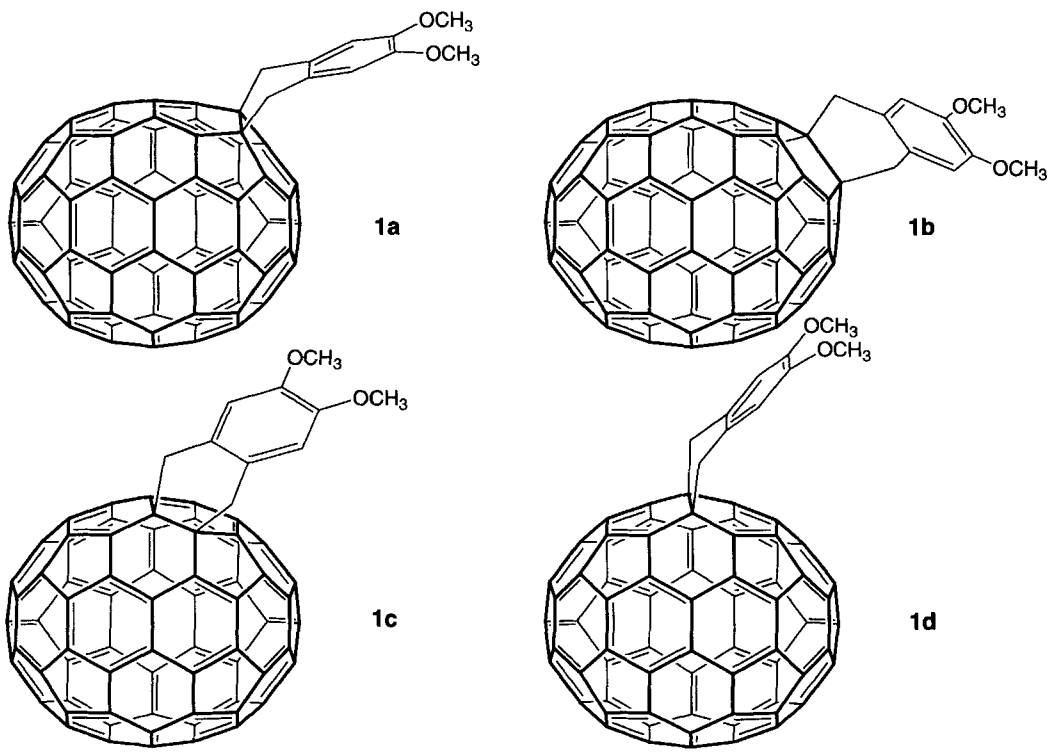


Fig. 5. *Structures of the four possible [6,6] monoadducts* **1** *of* C_{70}

monoadducts **1a**, **1b**, and **1c**, present in a weight ratio of *ca.* 5:12:1, and of one pure C_{76} adduct (**2c**) (see *Fig. 4*); two additional fractions (*B* and *D* in *Fig. 4*) contained a mixture of another two and three C_{76} adducts, respectively.

2.4.2. *C_{70} Adducts.* Three out of the four possible isomers **1a–d** (*Fig. 5*) have been isolated. Isomer **1b** was the main product (24%), followed by **1a** (10%), and **1c** was obtained only in a very small quantity (1–2%). The formation of the equatorial adduct **1d** was not observed at all. Due to some remaining C_{60} in the starting material, small quantities of a C_{60} adduct were obtained as well. Thus, the nature and yields of the isolated products are in good agreement with the proposed bond-reactivity model.

Even if it is assumed that addition occurred at [6,6] bonds only [2] [12] [13], the NMR-spectroscopic deduction of the structure of the three isomeric C_{70} adducts seemed not to be trivial at first view. The effect of conformational mobility on symmetry, however, allowed an unambiguous structural assignment by ^{1}H-NMR spectroscopy. The *Diels-Alder* reaction resulted in the formation of a cyclohexene ring that can interconvert between two boat conformations. At room temperature, this phenomenon was slow on the NMR time scale, but it became fast at *ca.* 80°. As a consequence, the average symmetry of the adducts, as it appears through NMR spectroscopy, is predicted to change on the transition from below to above coalescence temperature (T_c) in the case of isomers **1b** ($C_1 \rightarrow C_s$) and **1d** ($C_2 \rightarrow C_{2v}$), whereas **1a** (C_s) and **1c** (C_1) should keep the same symmetry. In fact, the combination of the symmetry behavior below and above T_c is unique for each isomer **1a–d**, thus allowing an unambiguous ^{1}H-NMR-spectroscopic assignment (*Table 2*).

Table 2. *Symmetry of the Four Possible [6,6] Adducts of C_{70}, as It Appears Through NMR Spectroscopy below and above Coalescene Temperature (T_c)*

	1a	**1b**	**1c**	**1d**
$T < T_c$	C_s	C_1	C_1	C_s
$T > T_c$	C_s	C_s	C_1	C_{2v}

Isomers **1a** and **1b** both exhibited C_s symmetry at $T > T_c$, but upon cooling, only **1a** retained this symmetry, whereas **1b** became C_1-symmetric. The characterization of adduct **1c** was more difficult, partly because of the small quantities available. Its assignment was based on the fact that eight peaks (2 *AB* systems) were observed below and above T_c for the 2 CH_2 groups. The MeO groups as well as the aromatic protons just showed a single signal each, regardless of temperature, but a broadening at low temperature suggested a peak overlap in this case. As none of the isomers exhibited the symmetry combination C_s ($T < T_c$)/C_{2v} ($T > T_c$), formation of the equatorial adduct **1d** could be excluded. Upon cooling to −20°, the integral ratio of the ^{1}H-NMR signals corresponding to the aromatic protons of the two conformers of **1a** was found to be 1.2:1, a value that corresponds to a small energy difference of $\Delta G = 0.07$ kcal/mol (= 0.29 kJ/mol).

The coalescence temperature as well as the energy barrier between the two conformers have been determined [16] for the major C_{70} adducts **1a** and **1b** as well as for the corresponding C_{60} adduct 1,2-dihydro-64,65-dimethoxy-1,2-(methano[1,2]benzeno-methano)fullerene[60] [12b]. The values of **1a** (T_c 320 K, $\Delta G^{\neq} = 15.3$ kcal/mol) were obtained from the coalescence of the aromatic signals, which showed no coupling. In the cases of **1b** (T_c 305 K, $\Delta G^{\neq} = 14.7$ kcal/mol) and the C_{60} adduct, the determination of T_c

was based on the resonance of the CH_2 groups. The inversion barriers of both C_{70} derivatives were similar to those of comparable C_{60} adducts [12b] [13a] (*Table 3* and *Fig. 6*).

Table 3. *Energy Barriers and Coalescence Temperatures (T_c) for the Cyclohexene Boat-to-Boat Interconversion of C_{70} Adducts* **1a** *and* **1b**, *and of the Corresponding C_{60} Derivative*

	C_{60} Adduct[a])	**1a**	**1b**
T_c [K]	318.1 ± 2	320.1 ± 2	305.1 ± 2
$\Delta G^{\neq}$ [kJ/mol]	63.3 ± 0.5	63.9 ± 0.5	61.6 ± 0.5
$\Delta G^{\neq}$ [kcal/mol]	15.1 ± 0.1	15.3 ± 0.1	14.7 ± 0.1

[a]) 1,2-Dihydro-64,65-dimethoxy-1,2-(methano[1,2]benzenomethano)fullerene[60] [12b]. A value of $\Delta G^{\neq} = 14.6$ kcal/mol was reported for a similar *Diels-Alder* adduct of C_{60} [13a].

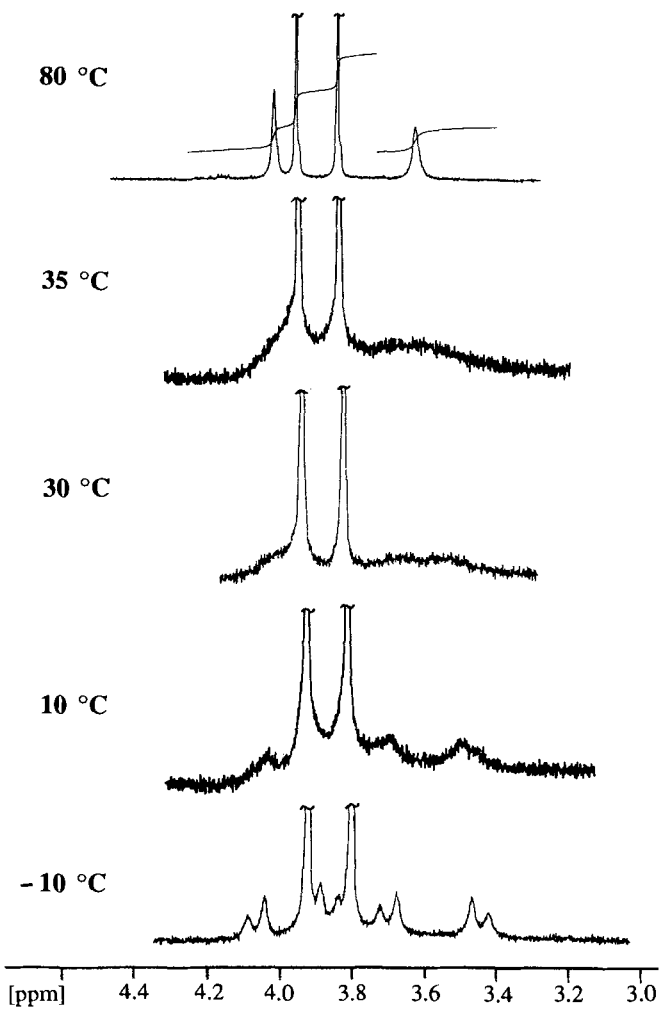


Fig. 6. *Aliphatic region of the 300-MHz ^{1}H-NMR spectrum ($C_2D_2Cl_4$) of* **1b** *at different temperatures.* The two strong peaks are the MeO resonances; the coalescing peaks belong to the 2 CH_2 groups.

The assignment of structures **1a** and **1b** by ^{1}H-NMR spectroscopy was confirmed through analysis of their ^{13}C-NMR spectra at 80°. Even though at this temperature both isomers exhibited C_s symmetry, the number of fullerene resonances differs, being dependent on the number of C-atoms located in the symmetry plane. In **1a**, 4 sp^2-C-atoms are in the plane, giving a total of 36 sp^2-C-atom resonances, whereas in **1b**, 2 sp^2-C-atoms and 2 sp^3-C-atoms are included in the plane, giving a total of 35 sp^2-C-atom resonances. In the spectrum of **1a**, all expected 36 fullerene sp^2-C-atom resonances were found in the region between 120 and 160 ppm. In addition, the MeO groups, the fullerene sp^3-C-atoms, and the CH_2 groups each gave one peak, and three signals were found for the benzene-ring C-atoms. The spectrum of **1b** showed a total of 39 resonances between 110 and 160 ppm. In this region, a maximum of 41 peaks is expected for 35 fullerene sp^2-C-atom resonances and the six benzene resonances, if the latter all appear at different chemical shift. In addition, the MeO groups, the fullerene sp^3-C-atoms, and the CH_2 groups showed six signals, two for each group. The small quantities of **1c** did not allow characterization by ^{13}C-NMR spectroscopy.

After heating the pure C_{70} adducts in 1,2-dichlorobenzene under Ar at 200° for 12 h, no evidence for isomerization or *retro*-addition was obtained by HPLC analysis. This result once more underlines the stability of the products resulting from a kinetically controlled *Diels-Alder* reaction with *o*-quinodimethane intermediates leading to the formation of an aromatic ring system. On the other hand, when solutions of the fullerene adducts were left at the atmosphere for several days, considerable decomposition took place which is probably due to reaction with oxygen as is suggested by the MALDI-TOF (matrix-assisted laser-desorption-ionization time-of-flight) mass-spectrometric analysis.

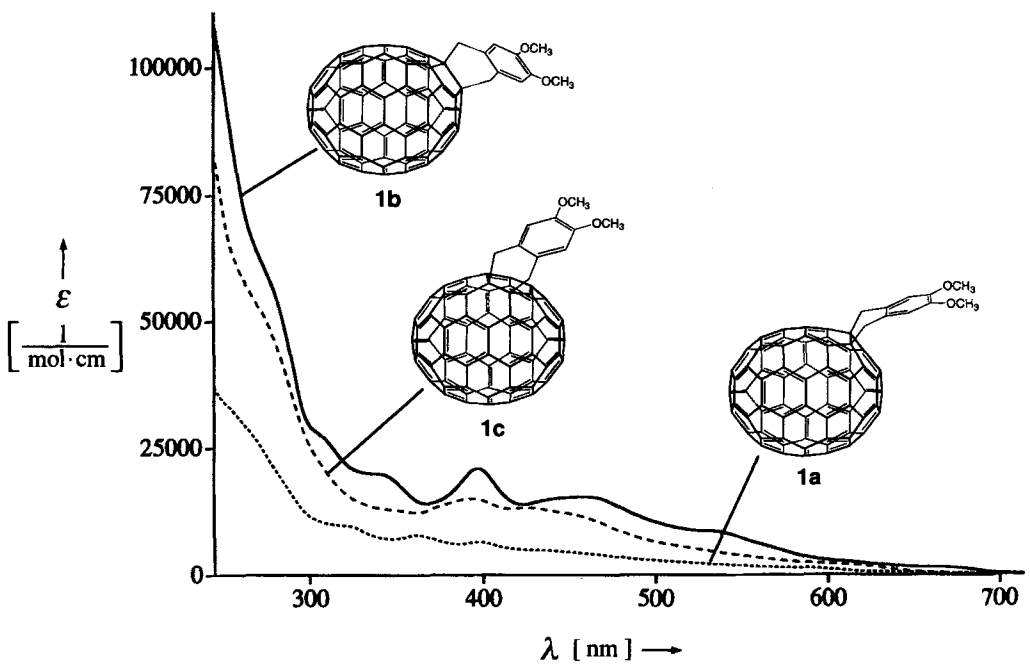


Fig. 7. *UV/VIS Spectra* (CH_2Cl_2) *of* C_{70} *adducts* **1a–c**

The UV/VIS spectra of the three isolated C_{70} isomers resembled each other in their general appearance, but the extinction coefficients of the absorption bands differed largely (*Fig. 7*). A difference in the color intensity of equimolar solutions of the two red isomers **1a** and **1b** in CH_2Cl_2 was clearly visible by naked eye. A characteristic maximum between 390 and 400 nm was observed for all three adducts, with extinction coefficients varying between 6600 $l \cdot mol^{-1} \cdot cm^{-1}$ (**1a**) and 21300 $l \cdot mol^{-1} \cdot cm^{-1}$ (**1b**). As opposed to the corresponding C_{60} derivative, **1a–c** exhibited a larger similarity in their spectra to the parent fullerene; in particular the onset of the optical absorption (*ca.* 700 nm) did not change upon transformation of C_{70} to its derivatives.

It should be noted finally, that adduct **1a** was considerably less soluble in CH_2Cl_2 than the other two isomers.

2.4.3. *C_{76} Adducts.* After isolation, structure determination [11c], and enantiomer separation [10] of chiral D_2-C_{76} have already been reported, we now describe the first characterization of a pure C_{76} derivative. The *Diels-Alder* reaction of 1,2-bis(bromomethyl)-4,5-dimethoxybenzene with C_{76} (*Scheme*) led to the formation of at least six isomers which were separated into four fractions (*A–D*) by HPLC (*Fig. 4b*). The major adduct **2c** was obtained in pure form and could be fully characterized. Five other isomers were obtained as a mixture of two (**2a,b**) and three (**2d,e,f**) isomers, respectively, and characterized by ^{1}H-NMR spectroscopy.

As a consequence of the D_2-symmetry of C_{76}, 3 out of 15 possible monoadducts, namely those in which addition took place across a bond lying on a C_2 axis (C(1)–C(6), C(29)–C(48), and C(33)–C(34); *Fig. 1*) are supposed to exhibit C_2 symmetry through NMR spectroscopy at $T > T_c$. All other isomers should appear to be C_1-symmetric above as well as below T_c. From the 76 resolved ^{13}C-NMR signals (out of 74 fullerene and a maximum of 6 benzene resonances) observed at 80° in the 110–160 ppm region, it can be concluded that **2c** belongs to the latter category (*Fig. 8*). The corresponding ^{1}H-NMR

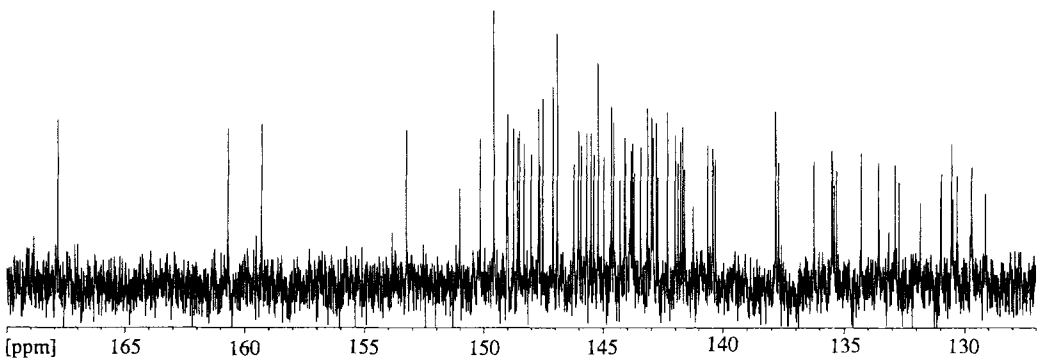


Fig. 8. *Expansion of the fullerene region of the 125.8-MHz ^{13}C-NMR spectrum* ($C_2D_2Cl_4$, 80°) *of C_{76} adduct* **2c**

spectrum confirmed the C_1 symmetry by showing a total of eight lines (2 *AB* systems) for the CH_2 groups and two peaks for each of the MeO and the aromatic protons, respectively.

Even if for reasons of symmetry a structural assignment was more difficult than in the case of the C_{70} adducts, we can again assume that in C_{76} the bonds with the highest local curvature are the most reactive. Two different, highly curved bonds (type α) can be found

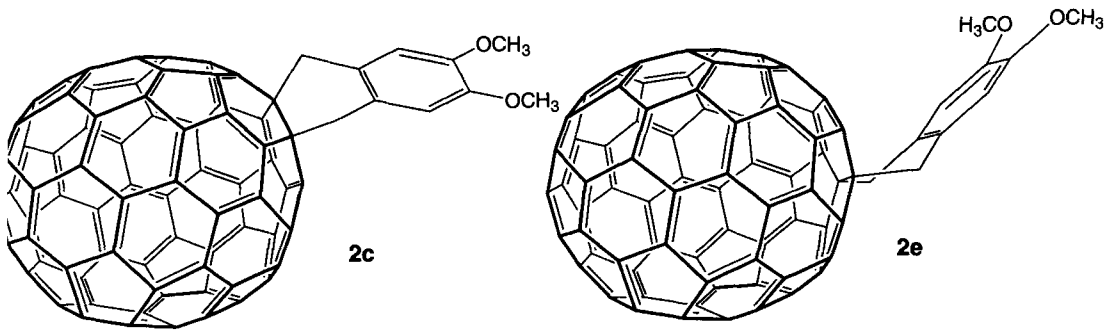


Fig. 9. *Proposed structural assignment of C_{76} adducts* **2c** *and* **2e**

at the poles of the molecule (*Fig. 3*); one of them (C(1)–C(6)) is lying on a C_2 axis, and the corresponding adduct should be C_2-symmetric; the other one (C(2)–C(3)) – actually involving the most pyramidalized C-atoms [10] – gives rise to a C_1-symmetric adduct. These considerations, together with the NMR-spectroscopic results, strongly suggest the assignment of structure **2c** to the major product of the *Diels-Alder* reaction with C_{76} (*Fig. 9*).

In the second most abundant product fraction *D* (see *Fig. 4b*), three isomers were distinguished by ^{1}H-NMR spectroscopy (*Fig. 10*). The major isomer **2d** again exhibited

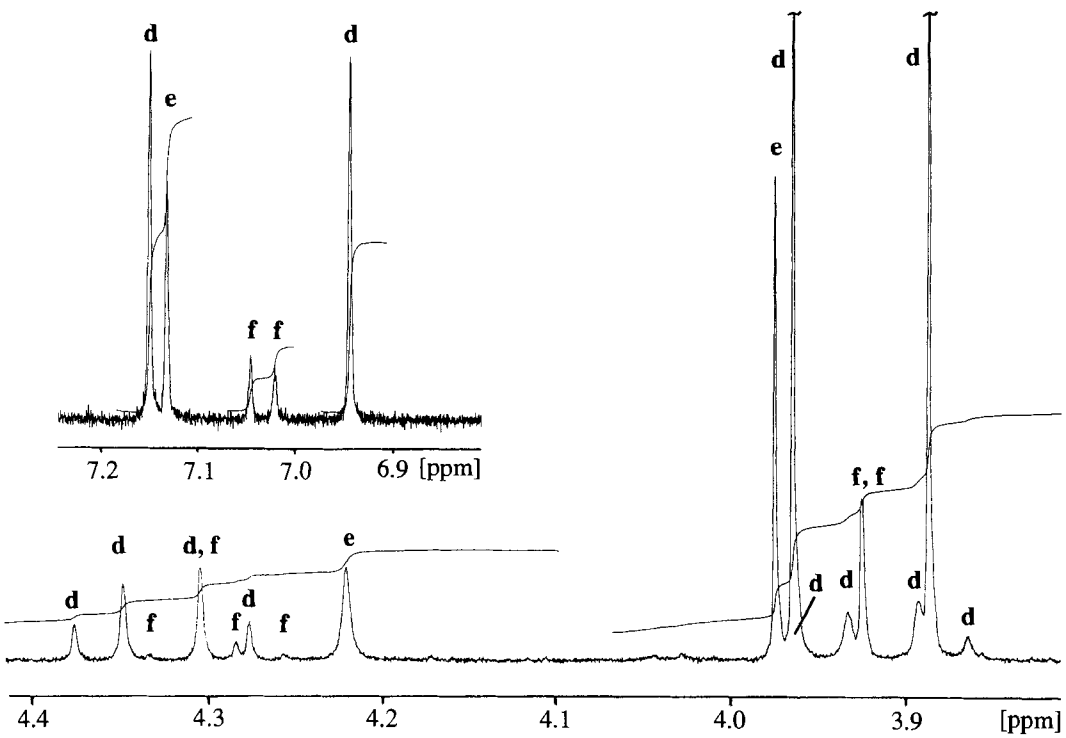


Fig. 10. *Expansions of the 500-MHz ^{1}H-NMR spectrum* ($C_2D_2Cl_4$, 80°) *of C_{76}-adduct fraction* D of **2** (*cf. Fig. 4b*)

C_1-symmetry on the NMR time scale at 80°, whereas the second one, **2e**, was C_2-symmetric. In the latter case, addition must have occurred at a bond lying on one of the C_2 axes of C_{76}. Since atoms 1 and 6 show a much higher pyramidalization angle (bond type α) than the atoms of the other two bonds lying on a symmetry axis (bond types κ and o), it can be assumed with confidence that adduct **2e** is the 1,6-isomer. A single resonance at 7.13 ppm (aromatic protons), together with another at 3.97 ppm (MeO groups) and a *s* at 4.22 ppm (CH_2 groups) was in accordance with this assignment. A small amount of a third isomer with C_1 symmetry was found as the minor component **2f** of fraction *D*. The ratio of the three isomers was determined by ^{1}H-NMR peak integration to 5.5:1.8:1.

Fraction *B* finally contained the two C_1-symmetric isomers **2a** and **2b** in a ratio of 1.5:1.

The colors of the different C_{76}-adduct fractions varied from yellow (fraction *B*), to green (fraction *C*), and to cognac (fraction *D*). Similarly to the parent fullerene, the onset of the electronic absorption of C_{76} adduct **2c** was located around 880 nm (*Fig. 11*),

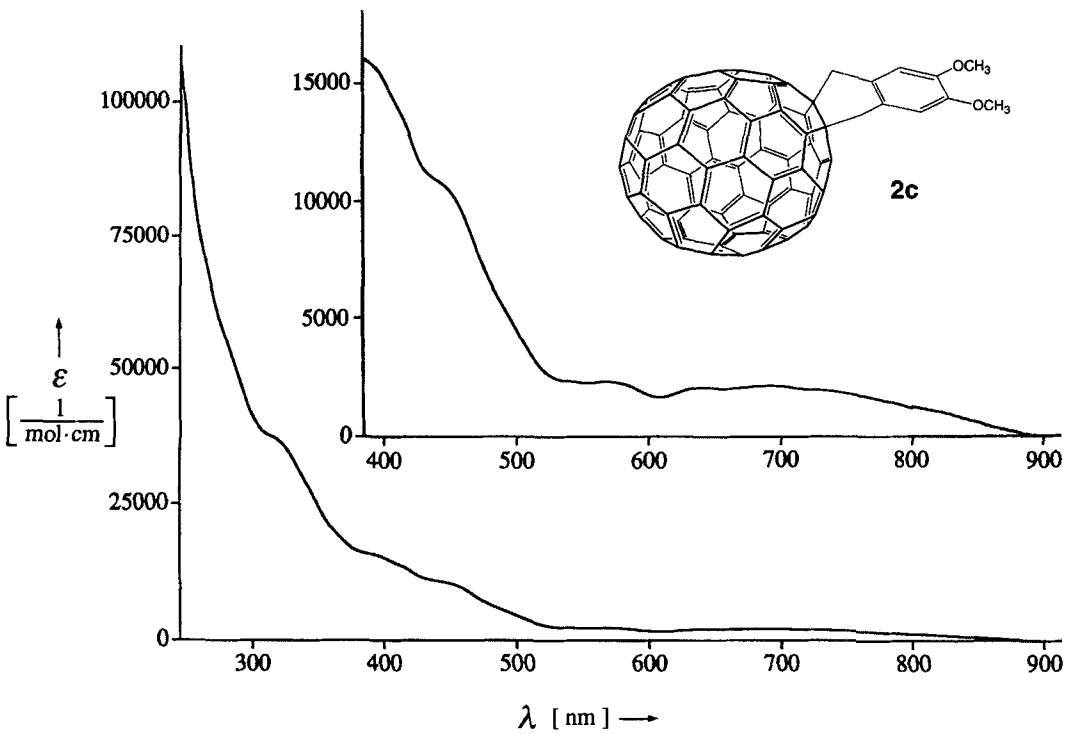


Fig. 11. *UV/VIS Spectrum* (CH_2Cl_2) *of* C_{76} *adduct* **2c**

whereas C_{70} and its derivatives showed no significant band above 700 nm. Absorption above 800 nm is important for fullerene-photosensitized generation of $^1O_2$ *in vivo*, as it is used in photodynamic therapy [17].

3. Conclusion. – *Diels-Alder* addition of an *o*-quinodimethane derivative to C_{70} and C_{76} led to the formation of several regioisomers which could be completely (C_{70} adducts)

or partly (C_{76} adducts) separated by prep. HPLC on a π-acidic *Buckyclutcher I* stationary phase.

The fact that the number of obtained monoadducts was smaller than the number of theoretically possible isomers demonstrates that even the very reactive diene used here showed regioselectivity to a certain extent. In accordance with the work of other authors [3–5], addition to C_{70} mainly occurred at the poles of the fullerene (high local curvature), whereas addition at the equator [6] (low local curvature) was not observed.

An unambiguous structural assignment of the three C_{70} adducts was based on ^{1}H-NMR spectroscopic investigations of temperature-dependent changes of the average molecular symmetry due to conformational mobility. The 1,9-adduct **1b** was found to be the most abundant isomer, followed by the 7,8-adduct **1a**. A third isomer, a 22,23-adduct **1c**, was isolated for the first time.

In the case of C_{76}, ^{1}H-NMR spectroscopy, together with the consideration of bond reactivities modulated by local curvature led to the assignment of the C_1-symmetric 2,3-adduct structure **2c** to the major cycloaddition product which was isolated in pure state. The same reasoning strongly suggested the structure of a 1,6-adduct for a C_2-symmetric derivative **2e** identified in a mixed fraction with two C_1-symmetric isomers (**2d, f**). A third fraction contained two other isomers (**2a, b**) of C_1-symmetry.

To predict the most reactive sites in higher fullerenes, a qualitative model for the evaluation of local curvature, taking account of the distribution of pentagons in the local environment of a given [6,6] bond, was developed. As it follows from the observed product ratio of *ca.* 12:5:1 for the 1,9-, 7,8-, and 22,23-isomers **1a–c** obtained from C_{70}, this simple model was found to be more accurate than the consideration of π-bond orders. On the other hand, the model as well as the experimental results described here correlate well with calculated pyramidalization angles [5c] [10] [14].

Experimental Part

General. Reagents used were reagent-grade commercials. HPLC Solvents were from *Biosolve*, *Fluka*, and *Merck*. Crude fullerene-rich soot containing *ca.* 5% soluble fullerenes was purchased from *Polygon Enterprises*, P.O. Box 5536 Waco, TX 76708, USA. The soot extract enriched in higher fullerenes was from *Hoechst AG*, Frankfurt am Main, Germany. The percentages of the individual fullerenes in the mixture were determined from the integrated HPLC peak areas in a separation on a reversed-phase C_{18} column with optical detection at $\lambda = 310$ nm: C_{60} *ca.* 35.4%, C_{70} *ca.* 20.8%, C_{76} *ca.* 15.7%, C_{78} *ca.* 6.0%, and C_{84} *ca.* 21%. C_{70} used for the transformations was isolated according to the procedure described in [1b]; the synthesis of 1,2-bis(bromomethyl)-4,5-dimethoxybenzene and 1,2-dihydro-64,65-dimethoxy-1,2-(methano[1,2]benzenomethano)fullerene[60] was reported in [12b]. For C_{76}, see HPLC. Toluene used for *Diels-Alder* reactions was dried over molecular sieves (4 Å). Thin layer chromatography: *Polygram SIL G/UV$_{254}$* from *Macherey-Nagel*. Column chromatography: Silica gel (0.05–0.10 mm, 140–270 mesh) from *Macherey-Nagel*. HPLC: *Vydac 201TP54 RP-C$_{18}$* (5 µm, 250 mm × 4.6 mm i.d.), *Shandon Hypersil-CTA* (5 µm, 250 mm × 4.6 mm i.d.), and *Regis Buckyclutcher I Trident-Tri-DNP* (5 µm, 250 mm × 4.6 mm i.d., and 10 µm, 500 mm × 21.1 mm i.d.) columns; *Knauer HPLC Pump 64* high-pressure gradient pumps with anal. pump heads and vacuum on-line degasser, electrical injection valve *AA A0619*, and *Variable-Wavelength Monitor* UV/VIS detector from *Knauer*; all chromatograms were taken at r.t. with the detector wavelength fixed at λ 310 nm. Anal. HPLC: flow rate 1 ml/min, injection of 10 µl of the soln. of higher fullerenes in toluene (see below); prep. HPLC: injection of 800 µl of the soln. of higher fullerenes in 1,2-dichlorobenzene (*o*-DCB) (see below) onto the *Buckyclutcher I* prep. column, hexane/toluene 3:2, flow rate 8 ml/min, collection of fractions of C_{60}, C_{70}, C_{76}/C_{78}, C_{78}/C_{76}, and C_{84}; reinjection of the C_{76} fraction under the same conditions yielded 97% pure C_{76} used for the transformations. UV/VIS Spectra: *Varian-CARY-5* spectrometer. ^{1}H- and ^{13}C-NMR Specta: *Bruker-AMX-500* and *Varian-GEMINI-200* and *-300* spectrometers. MS: MALDI-TOF spectra with

reflectron detection were measured in the positive-ion mode, acceleration voltage 10 kV, on a *Bruker REFLEX* spectrometer; 2,5-dihydroxybenzoic acid (0.1M in MeCN/EtOH/H_2O 50:45:5) was used as a matrix.

Prepurification of Higher Fullerenes for HPLC. a) Soot extract (4.8 mg) enriched in higher fullerenes was dissolved in toluene (5 ml) and separated from a baseline by flash chromatography (silica gel, toluene). The obtained soln. was used for anal. HPLC. *b*) Solns. for prep. HPLC were prepared in batches of 90–100 mg of soot extract dissolved in 9–10 ml of *o*-DCB and chromatographed on a short silica-gel column with the same solvent.

Diels-Alder *Reaction of* C_{70}. C_{70} (43.3 mg, 0.052 mmol) and (Bu_4N)I (58.0 mg, 0.157 mmol) were dissolved in dry toluene (30 ml). Then 1,2-bis(bromomethyl)-4,5-dimethoxybenzene (23.0 mg, 0.071 mmol) was added and the soln. refluxed under Ar for 27 h. After cooling to r.t., the product was washed (H_2O) and the org. phase filtered. The concentrated filtrate was chromatographed (SiO_2, toluene/hexane 3:1) to give 23 mg (53%) of unreacted C_{70} and 19 mg (37%) of monoadduct isomers **1**. Higher adducts were eluted with toluene/hexane/acetone 3:1:1. The monoadduct fraction **1** was dissolved in *o*-DCB and submitted to prep. HPLC (*Buckyclutcher I*, CH_2Cl_2/hexane 3:2, flow rate 8 ml/min): C_{60} adduct (small amount) and 3 fractions of C_{70} monoadducts which were reinjected under the same conditions to give the pure isomers **1a–c**.

7,8-Dihydro-74,75-dimethoxy-7,8-(methano[1,2]benzenomethano)fullerene[70] (**1a**): 5.4 mg (10%). R_f (toluene/hexane 3:1) 0.17. UV/VIS (CH_2Cl_2): 645 (sh, 700), 596 (sh, 1500), 537 (sh, 2200), 452 (sh, 4600), 438 (sh, 5000), 397 (6600), 370 (sh, 7400), 362 (8000), 326 (sh, 9500), 274 (sh, 24100), 254 (sh, 33000). ^{1}H-NMR (300 MHz, $C_2D_2Cl_4$, 393 K): 6.82 (*s*, 2 arom. H); 3.85 (*s*, 2 MeO); 3.67 (*d*, *J* = 13.8, 1 CH_2); 3.49 (*d*, *J* = 13.8, 1 CH_2). ^{1}H-NMR (300 MHz, $C_2D_2Cl_4$, 253 K): 6.93 (*s*, 1 arom. H); 6.56 (*s*, 1 arom. H); 3.91 (*s*, 1 MeO); 3.84–3.60 (*m*, 1 CH_2); 3.66 (*s*, 1 MeO); 3.54–3.32 (*m*, 1 CH_2). ^{13}C-NMR (125.8 MHz, $C_2D_2Cl_4$, 353 K): 155.61; 155.26; 154.64; 151.88; 150.87; 150.55; 149.51; 149.49; 149.42; 149.27; 149.22; 148.46; 148.23; 147.99; 147.38; 147.20; 147.17; 146.99; 146.79; 146.76; 146.32; 146.12; 145.38; 145.18; 144.80; 144.65; 143.97; 142.33; 141.56; 140.89; 132.73; 132.45; 131.65; 131.57; 129.90; 129.30; 128.48; 126.21; 112.79 (CH); 56.89 (MeO); 56.49 (fullerene sp^3-C); 43.84 (CH_2). MS (MALDI-TOF): 1004.9 (M^+), 839.4 ($[C_{70}]^+$).

1,9-Dihydro-74,75-dimethoxy-1,9-(methano[1,2]benzenomethano)fullerene[70] (**1b**): 12.2 mg (24%). R_f (toluene/hexane 3:1) 0.17. UV/VIS (CH_2Cl_2): 676 (sh, 1300), 610 (sh, 2700), 567 (sh, 5500), 538 (sh, 8500), 459 (15600), 439 (sh, 15000), 397 (21300), 346 (sh, 19700), 308 (sh, 27600), 278 (sh, 57800). ^{1}H-NMR (300 MHz, $C_2D_2Cl_4$, 353 K): 7.07 (*s*, 1 arom. H); 6.84 (*s*, 1 arom. H); 4.01 (*s*, 1 CH_2); 3.95 (*s*, 1 MeO); 3.84 (*s*, 1 MeO); 3.62 (*s*, 1 CH_2). ^{1}H-NMR (300 MHz, $C_2D_2Cl_4$, 263 K): 7.03 (*s*, 1 arom. H); 6.80 (*s*, 1 arom. H); 4.07 (*d*, *J* = 14.0, 1 H, CH_2); 3.92 (*s*, 1 MeO); 3.86 (*d*, *J* = 14.0, 1 H, CH_2); 3.80 (*s*, 1 MeO); 3.70 (*d*, *J* = 14.0, 1 H, CH_2); 3.45 (*d*, *J* = 14.0, 1 H, CH_2). ^{13}C-NMR (125.8 MHz, $C_2D_2Cl_4$, 353 K): 161.77; 155.40; 151.73; 151.70; 151.51; 151.00 (2×); 150.23; 150.20; 150.15; 149.73 (2×); 149.60; 149.36; 149.14; 148.74; 147.77; 147.35 (2×); 146.67; 146.00; 143.46; 143.34; 143.26; 143.10; 140.77; 140.52; 137.29; 134.21; 134.13; 131.73; 131.61; 129.52; 129.50; 129.30; 128.47; 125.58; 113.09 (CH); 112.96 (CH); 59.88 (fullerene sp^3-C); 58.10 (fullerene sp^3-C); 57.00 (MeO); 56.90 (MeO); 45.05 (CH_2); 41.40 (CH_2). MS (MALDI-TOF): 1005.3 (M^+), 840.2 ($[C_{70}]^+$).

22,23-Dihydro-74,75-dimethoxy-22,23-(methano[1,2]benzenomethano)fullerene[70] (**1c**): *ca.* 0.5–1.0 mg (1–2%). R_f (toluene/hexane 3:1) 0.17. UV/VIS (CH_2Cl_2): 663 (sh, 400), 619 (sh, 1900), 449 (sh, 12100), 427 (13100), 393 (16200), 377 (sh, 13700), 317 (sh, 17100), 275 (sh, 50500). ^{1}H-NMR (300 MHz, $C_2D_2Cl_4$, 353 K): 7.07 (*s*, 1 arom. H); 6.94 (*s*, 1 arom. H); 4.08 (*d*, *J* = 13.5, 1 H, CH_2); 3.97 (*s*, 1 MeO); 3.87 (*s*, 1 MeO); 3.86 (*d*, *J* = 13.5, 1 H, CH_2); 3.75 (*d*, *J* = 13.5, 1 H, CH_2); 3.50 (*d*, *J* = 13.5, 1 H, CH_2). ^{1}H-NMR (300 MHz, $C_2D_2Cl_4$, 253 K); 7.04 (*s*, 1 arom. H); 6.90 (*s*, 1 arom. H); 4.06 (*d*, *J* = 13.8, 1 H, CH_2); 3.94 (*s*, 1 MeO); 3.83 (*s*, 1 MeO); 3.68 (*d*, *J* = 13.8, 1 H, CH_2); 3.58 (*d*, *J* = 13.8, 1 H, CH_2); 3.45 (*d*, *J* = 13.8, 1 H, CH_2). MS (MALDI-TOF): 1004.8 (M^+).

Diels-Alder *Reaction of* C_{76}. As described for C_{70}, with C_{76} (26.7 mg, 0.029 mmol), (Bu_4N)I (35.3 mg, 0.096 mmol), toluene (20 ml), and 1,2-bis(bromomethyl)-4,5-dimethoxybenzene (14.1 mg, 0.044 mmol). Column chromatography (SiO_2, toluene/hexane 3:1) gave 4.0 mg (15%) of unreacted C_{76} and 10.5 mg (33%) of monoadducts **2**. Higher adducts were eluted with toluene/hexane/acetone 3:1:1. The monoadduct fraction **2** was dissolved in CH_2Cl_2 and separated by prep. HPLC (*Buckyclutcher I*, see above). Four fractions *A–D* were collected. Each was rechromatographed under the same conditions to give 0.5 mg (2%) of fraction *A*, 0.9 mg (3%) of fraction *B*, 4.6 mg (15%) of fraction *C*, and 4.5 mg (14%) of fraction *D*. ^{1}H-NMR(353 K) showed that fraction *B* contained the C_1-symmetric isomers **2a, b**, fraction *C* the C_1-symmetric isomer **2c**, and fraction *D* the C_2-symmetric and the 2 C_1-symmetric isomers **2e** and **2d, f**, resp. Fraction *A* was too small and its separation from fraction *B* not good enough for further analysis.

Dihydro-80,81-dimethoxy(methano[1,2]benzenomethano)fullerene[76] (**2a, b**): 0.9 mg (3%). R_f (toluene/hexane 3:1) 0.17. ^{1}H-NMR (500 MHz, $C_2D_2Cl_4$, 353 K): 7.04 (*s*, 1 arom. H (**2a**)); 7.01 (*s*, 1 arom. H (**2a**)); 6.94 (*s*, 1 arom. H (**2b**)); 6.88 (*s*, 1 arom.H (**2b**)); 4.44 (*d*, *J* = 13.6, 1 H, CH_2 (**2a**)); 4.38 (*d*, *J* = 13.6, 1 H, CH_2 (**2a**)); 4.05 (*d*,

J = 13.6, 1 H, CH_2 (**2a**)); 4.01 (*d*, J = 13.6, 1 H, CH_2 (**2a**)); 3.91 (2*s*, 2 MeO (**2a**)); 3.88 (*s*, 1 MeO (**2b**)); 3.85 (*s*, 1 MeO (**2b**)); 3.77 (*d*, J = 13.6, 1 H, CH_2 (**2b**)); 3.68 (*d*, J = 13.6, 1 H, CH_2 (**2b**)); 1 CH_2 (**2b**) not assigned. MS (MALDI-TOF): 1076.5 (M^+), 911.7 ($[C_{76}]^+$).

2,3-Dihydro-80,81-dimethoxy-2,3-(methano[1,2]benzenomethano)fullerene[76] (**2c**): 4.6 mg (15%). R_f (toluene/hexane 3:1) 0.17. UV/VIS (CH_2Cl_2): 800 (1200), 692 (2100), 641 (2000), 568 (2300), 453 (sh, 10200), 412 (sh, 13800), 353 (sh, 22400), 321 (sh, 35800), 266 (sh, 68200). ^{1}H-NMR (500 MHz, $C_2D_2Cl_4$, 353 K): 6.97 (*s*, 1 arom. H); 6.88 (*s*, 1 arom. H); 3.98 (*d*, J = 12.0, 1 H, CH_2); 3.93 (*d*, J = 12.0, 1 H, CH_2); 3.89 (*s*, 1 MeO); 3.86 (*s*, 1 MeO); 3.84 (*d*, J = 11.0, 1 H, CH_2); 3.78 (*d*, J = 11.0, 1 H, CH_2). ^{13}C-NMR (125.8 MHz, $C_2D_2Cl_4$, 353 K): 167.83; 160.67; 159.26; 153.24; 150.99; 150.14; 149.56 (2×); 149.01; 148.98; 148.75; 148.56; 148.49; 148.30; 147.99; 147.67; 147.63; 147.50; 147.07; 146.89 (2×); 146.20; 146.00; 145.90; 145.66; 145.48; 145.38; 145.19 (2×); 144.96; 144.65; 144.55; 144.28; 144.09; 144.06; 143.84; 143.77; 143.71; 143.44; 143.15; 142.98; 142.92; 142.78; 142.71; 142.31; 142.00; 141.88; 141.76; 141.68; 141.61; 141.23; 140.61; 140.41; 140.31; 137.82; 137.80; 137.69; 136.24; 135.49; 135.45; 135.39; 135.31; 134.27; 133.56; 132.85; 132.69; 131.81; 130.98; 130.95; 130.53; 130.48; 130.31; 129.70; 129.11; 113.08 (CH); 112.86 (CH); 61.13 (fullerene sp^3-C); 59.56 (fullerene sp^3-C); 56.95 (MeO); 56.91 (MeO); 45.00 (CH_2); 43.46 (CH_2); peaks at 66.07 and 29.85 were assigned to impurities. MS (MALDI-TOF): 1077.0 (M^+), 911.6 ($[C_{76}]^+$).

1,6-Dihydro-80,81-dimethoxy-1,6-(methano[1,2]benzenomethano)fullerene[76] (**2e**) *and Regioisomeric C_{76} Adducts* (**2d, f**): 4.5 mg (14%). R_f (toluene/hexane 3:1) 0.17. ^{1}H-NMR (500 MHz, $C_2D_2Cl_4$, 353 K): 7.15 (*s*, 1 arom. H (**2d**)); 7.13 (*s*, 2 arom. H (**2e**)); 7.05 (*s*, 1 arom. H (**2f**)); 7.02 (*s*, 1 arom. H (**2f**)); 6.94 (*s*, 1 arom. H (**2d**)); 4.37 (*d*, J = 13.9, 1 H, CH_2 (**2d**)); 4.32 (*d*, J = 13.9, 1 H, CH_2 (**2f**)); 4.29 (*d*, J = 13.9, 1 H, CH_2 (**2d**)); 4.27 (*d*, J = 13.9, 1 H, CH_2 (**2f**)); 4.22 (br. *s*, 4 H, CH_2 (**2e**)); 3.97 (*s*, 2 MeO (**2e**)); 3.96 (*s*, 1 MeO (**2d**)); 3.95 (*d*, J = 13.9, 1 H, CH_2 (**2d**)); 3.92 (2*s*, 2 MeO (**2f**)); 3.88 (*s*, MeO **2d**)); 3.88 (*d*, J = 13.9, 1 H, CH_2 (**2d**)); 1 CH_2 (**2f**) not assigned. MS (MALDI-TOF): 1077.8 (M^+), 911.5 ($[C_{76}]^+$).

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