72. Improved Purification of C_{60} and Formation of σ- and π-Homoaromatic Methano-Bridged Fullerenes by Reaction with Alkyl Diazoacetates

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(15.II.93)

A rapid and inexpensive method for the large-scale purification of C_{60} is the simple filtration of the toluene-soluble extract of commercial fullerene soot through a short plug of charcoal/silica gel with toluene as the eluent. Reactions of C_{60} with ethyl and *tert*-butyl diazoacetates in refluxing toluene lead to the formation of the (alkoxycarbonyl)methylene-bridged isomers **1a–3a** and **1b–3b**, respectively, which can be equilibrated, upon further heating, into the single compounds **1a** and **1b**, respectively. Isomers **1a/b** possess the methano bridge at the 6-6 ring junction, whereas structures **2a/b** and **3a/b** are bridged at the 6-5 junction. A dramatic influence of local and π-ring current anisotropic effects of the fullerene sphere on the NMR chemical shifts of the methine protons in the bridge is observed: the chemical shifts of the protons located over a pentagon ring in **2a/b** and over a hexagon ring in **3a/b** differ by $\Delta\delta = 3.47$ and 3.45 ppm, respectively. The analysis of the ^{13}C-NMR chemical shifts of the bridgehead C-atoms and the ^1J(C,H) coupling constants for the methano-bridge atoms reveals conclusively that the 6-5-ring-bridged structures **2a/2b** and **3a/3b** are π-homoaromatic ('open' transannular bond) and the 6-6-ring-bridged structures **1a/b** are σ-homoaromatic ('closed' transannular bond). The electronic absorption spectra show that π-homoconjugation in **2a/b** and **3a/b** represents a much smaller electronic perturbation of the original C_{60} chromophore than σ-homoconjugation in **1a/b**. The results of this study demonstrate an impressive linkage between the chemistry of methano-bridged annulenes and methano-bridged fullerenes.

1. Introduction. – Since the discovery of the macroscopic-scale fullerene synthesis by *Krätschmer, Huffman* and coworkers in 1990 [1], methods for the isolation and purification of buckminsterfullerene C_{60}, the most abundant component in the toluene-soluble extract of the fullerene soot obtained by resistive or arc-heating of graphite under He atmosphere, have been continuously improved. The earliest purification of C_{60} from C_{70} and the higher fullerenes involved flash chromatography of the crude fullerene extract on neutral alumina with hexane/toluene 95:5 (v/v) as the eluent [2]. A modification of this method allowed easier solvent recycling by performing the chromatography within a *Soxhlet* extractor and changing to pure hexane as the solvent [3]. As a disadvantage, however, a significant amount of decomposition occurs on the column during this process. More recent work described medium-pressure liquid chromatography (MPLC) separations of C_{60} and C_{70} on silica gel with hexane or on C_{18} reversed-phase silica gel with toluene/MeCN 75:25 (v/v) as the eluent [4]. Different high-performance liquid chromatography (HPLC) protocols have been worked out, and a variety of stationary phases have been used such as alkyl (C_{18}) and phenylsiloxane-based materials [5], *Pirkle*-type phases [6], and charge-transfer phases [6] [7]. Eluents most commonly used are hexane, either pure or in combination with a more polar component like CH_2Cl_2, Et_2O, THF, or an alcohol.

The major problem common to all of these early methods is the relative insolubility of the fullerenes in the mobile phase, a fact which limits the amount of material that can be

processed. Best solvents for fullerenes are CS_2 and benzene, as well as alkylated or halogenated aromatic solvents. With these solvents, however, the separation of C_{60} from the higher fullerenes on the stationary phases mentioned above is very poor. High-pressure gel-permeation chromatography combined with automated reinjection/sample collection was the first method which used pure toluene as the mobile phase and, as a result, was amenable to larger-scale purifications of C_{60} [8]. The ideal separation procedure, however, would allow one to use simple, inexpensive laboratory equipment and reagents and provide an efficient gram-scale separation within a short period of time. Recently, *Tour* and coworkers introduced a C_{60} purification method which meets almost all of these requirements [9]. By using a mixture of silica gel/carbon *Norit-A* 2:1 as stationary phase in a flash chromatography set-up at 7–10 psi head pressure, they achieved the separation of 1.85 g of fullerene extract in 1 h with a C_{60} yield of 63% out of a possible 75%. In this paper, we report a further simplification of the *Tour* method and describe an inexpensive plug-filtration method for the isolation of gram quantities of high-purity C_{60}.

Shortly after buckminsterfullerene had become available in larger quantities, synthetic chemists developed interest in its functionalization. Among the conversions which led to structurally defined monoaddition products are the reaction of C_{60} with diazoalkanes [10][11], diazirines [12], dienes [13], nucleophiles [14], and transition-metal complexes [15]. As part of ongoing efforts in Zurich to prepare H_2O-soluble fullerene derivatives with potential biological activity [12], we became interested in forming a C_{60}-monocarboxylic acid, which could subsequently be covalently attached to oligopeptides *via* amide-bond formation. For the desired functionalization, the reaction of C_{60} with ethyl diazoacetate, initially described in a review by *Wudl* [11], followed by hydrolysis, seemed most suitable. According to this preliminary report, the reaction proceeds *via* 1,3-dipolar cycloaddition to give the 1-pyrazoline as intermediate, which subsequently partitions to the 2-isomer and, under loss of nitrogen, to the bridged fullerene (*Scheme 1*). The scope of

Scheme 1
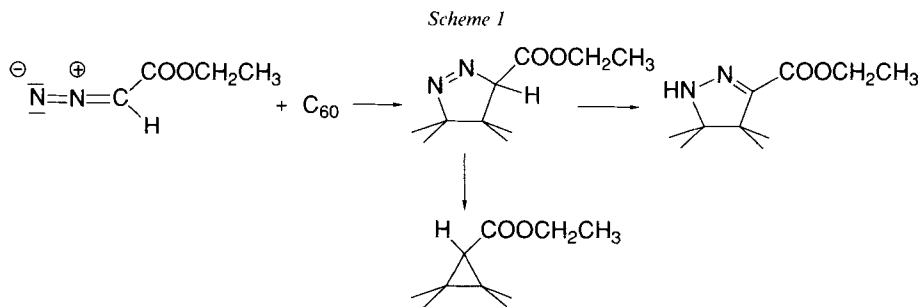
the reaction of C_{60} with diazo compounds seems quite broad: *Wudl* and coworkers prepared a variety of bridged fullerenes, which they named as 'fulleroids', by the addition of CH_2N_2 [16] or its mono- and diphenyl derivatives to C_{60} [10][11] and showed that this functionalization should also be applicable to the preparation of fullerene polymers [10b].

Here, we describe a detailed investigation of the reaction of alkyl diazoacetates with C_{60} in refluxing toluene and assign structures to the different bridged fullerenes formed under kinetic and thermodynamic control.

2. A Simple Purification of C$_{60}$. – The separation of C$_{60}$ from C$_{70}$ and the higher fullerenes by flash chromatography (7–10 psi) on a mixture of silica gel/*Norit-A* charcoal 2:1 with toluene as the eluent, which was recently reported by *Tour* and coworkers,
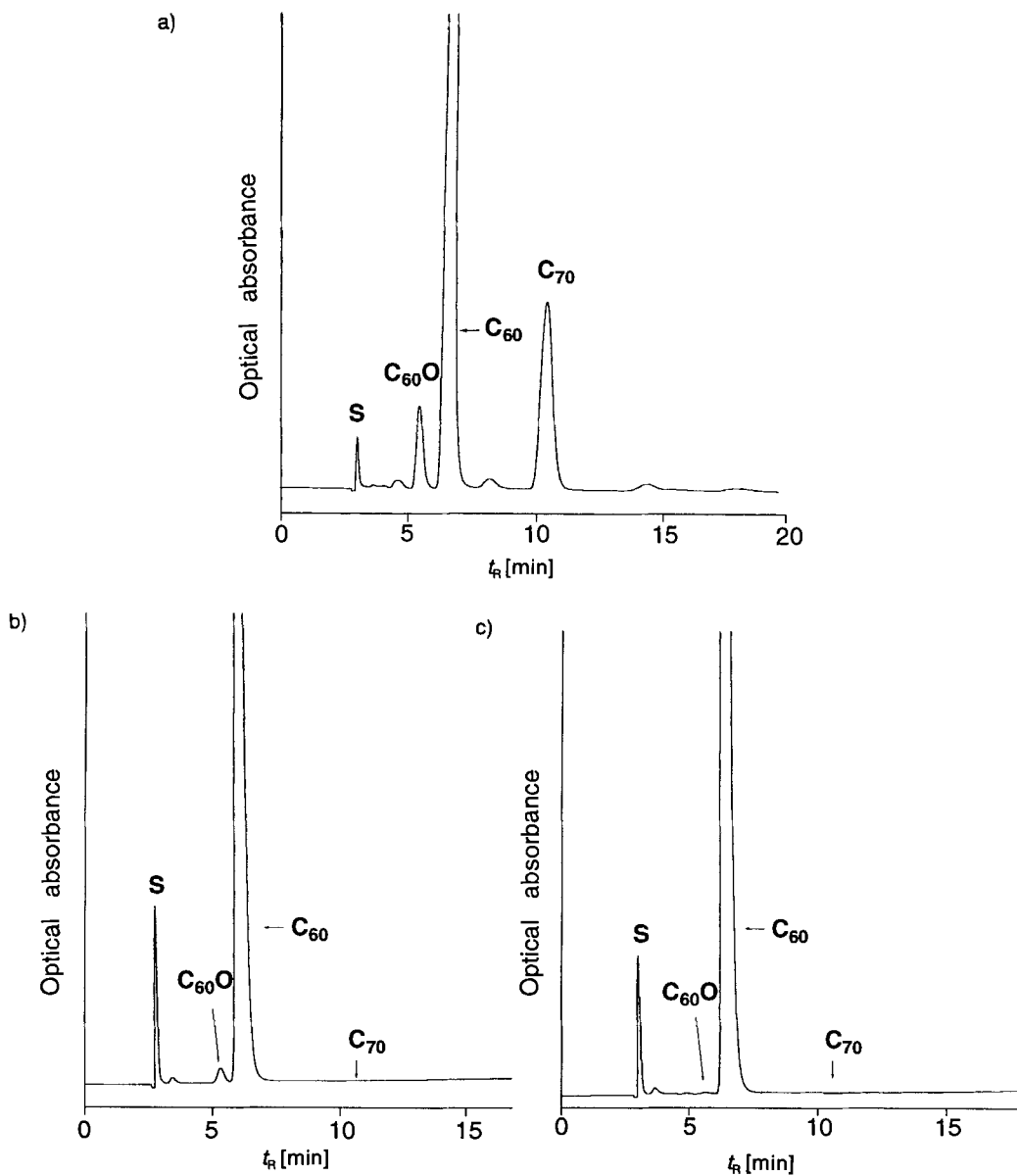

Fig. 1. *HPLC Profiles (C$_{18}$ reversed-phase, eluent: MeCN/toluene 1:1 (v/v), 310-nm UV detection) of a) the toluene-soluble extract of commercially available fullerene soot (Polygon Corporation), b) C$_{60}$ purified by filtration through a plug of silica gel/charcoal with a lower height-to-diameter ratio, and c) C$_{60}$ purified by filtration through a plug with a larger height-to-diameter ratio.* (S) = Solvent.

represents a major breakthrough in the large-scale preparation of pure C_{60} [9]. This method can be further simplified! We found activated, acid-washed charcoal *Darco G60* (*Fluka*), mixed with silica gel (*Merck*, 230–400 mesh, 0.040–0.063 mm), to be such an effective stationary phase for fullerene separation that flash chromatography is not necessary and can be replaced by a simple plug filtration. In our method, a fritted funnel (10-cm diameter) is covered with a slurry of 63 g of charcoal and 125 g of silica gel to give a plug of 5.5-cm height. A concentrated solution of soluble fullerene soot extract in toluene is loaded and eluted by the application of a slight vacuum at the filter flask. Only 15 min are necessary for the elution of 1.5 g of C_{60} starting from 2.54 g of fullerene soot extract. HPLC Analysis of the material shows no contamination (< 0.05%) by C_{70} or higher fullerenes. The only impurity in the purified C_{60} is 1–3% of $C_{60}O$ (*Fig. 1b*), which is formed during soot production [17] [18]. The commercial fullerene soots used for the experiments described in this paper contained up to 5% of $C_{60}O$ (*Fig. 1a*). For most chemical conversions, C_{60} which is free of any other fullerene and contains as sole impurity 1–3% of $C_{60}O$ is a suitable starting material. The *Fluka* charcoal used in this study seems to be much more active than the *Norit-A* alkaline decolorizing carbon originally used by *Tour* and coworkers [9]. Whereas some of the C_{70} present in the initial soot extract can be eluted from the carbon *Norit-A*/silica-gel mixture with toluene [9], this fullerene can only be partially removed from the *Fluka* charcoal/silica-gel plug by eluting with CS_2. Interestingly, previous attempts to use graphite as stationary phase had been much less successful: its retention capacity for fullerenes is much lower than that of activated charcoal [19].

If a $C_{60}O$-free sample is desired, a larger height-to-diameter ratio of the plug must simply be applied. Whereas $C_{60}O$ has a shorter retention time on C_{18} reversed phase (*Fig. 1*), it elutes after C_{60} from the charcoal/silica-gel mixture. With the larger plug, material of 99.75% purity (*Fig. 1c*) can be conveniently prepared within a short amount of time. The plug method is readily amenable to large-scale separations, and its negligible costs now make production or purchase of crude fullerene soot, rather than separation and purification, the most costly steps in the preparation of gram quantities of pure C_{60}.

3. Methano-Bridged Fullerenes by Reaction of C_{60} with Alkyl Diazoacetates. – In the synthesis of an (ethoxycarbonyl)methylene-bridged C_{60} as precursor for a fullerene-

1a R = CH₃CH₂
1b R =(CH₃)₃C

2a R = CH₃CH₂
2b R =(CH₃)₃C

3a R = CH₃CH₂
3b R =(CH₃)₃C
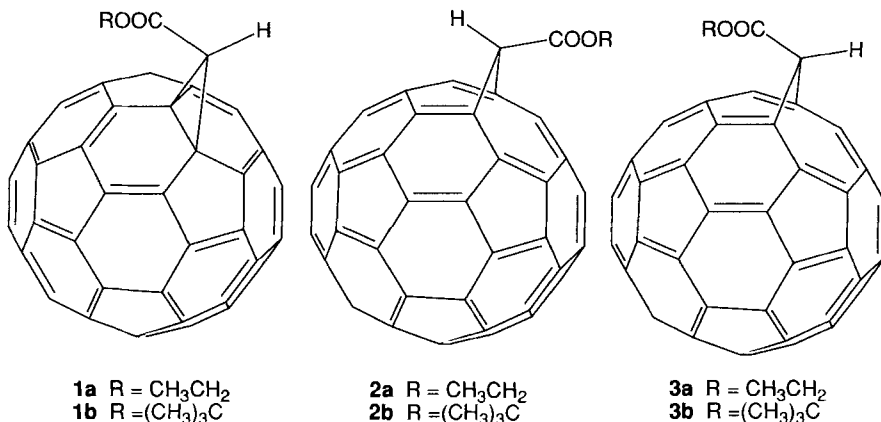
monocarboxylic acid, we initially stirred equimolar amounts of ethyl diazoacetate and C_{60} in toluene for several days at room temperature. Since the reaction proceeded sluggishly and with low conversion, we changed to refluxing toluene, which led to the disappearance of most of the starting material within 7 h. Chromatography on silica gel with hexane followed by hexane/toluene 1:1 (v/v) afforded residual C_{60} (R_f 0.82 in the 1:1 mixture) and one isolable purple product fraction which was shown in the following detailed ^{1}H- and ^{13}C-NMR analysis to be a mixture of the three (ethoxycarbonyl)methylene-bridged C_{60} isomers **1a–3a**, all with identical R_f values (0.43). No evidence for the formation of 1- or 2-pyrazoline-fused C_{60}, proposed in *Scheme 1* [11], was obtained in the reaction in refluxing toluene. The R_f values of these N-containing derivatives would have differed significantly from those of **1a–3a**. In the IR spectrum of the product fraction, the N=N stretching vibration of the 1-pyrazoline ring at 1560 cm^{-1} was absent. In addition, NMR and FAB-MS as well as combustion-analysis data (absence of N) supported the absence of isolable pyrazoline intermediates.

The ^{1}H-NMR spectrum of the mixture of **1a–3a** showed three sets of methine resonances at 4.31, 6.79, and 3.32 ppm in an approximate relative intensity ratio of 1:1:3, respectively (*Fig. 2a*). In addition, three sets of Et resonances, in a similar relative intensity ratio, are also present in the spectrum. Clearly, the (ethoxycarbonyl)methylene protons in each isomer are in a very different environment. When the isomeric mixture was heated to reflux in toluene for additional 24 h, the color of the solution changed from purple to pink-red. The only isolable product fraction again corresponds to monobridged fullerene (R_f 0.43) and gives a very simple ^{1}H-NMR spectrum (*Fig. 2b*) which only shows
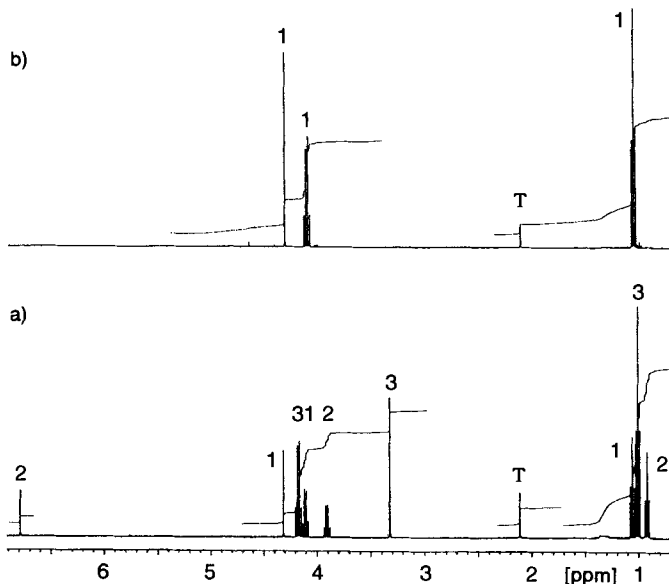

Fig. 2. *400-MHz ^{1}H-NMR Spectra recorded in C_6D_6 of* a) *the mixture of (ethoxycarbonyl)methylene-bridged fullerenes* **1a**, **2a**, *and* **3a** *in the approximate ratio of 1:1:3 and* b) *pure isomer* **1a**. T = Toluene.

isomer **1a** with the methine resonance at 4.31 ppm. Apparently, the initial reaction had produced under kinetic control a mixture of three isomers **1a–3a** which, upon further heating, equilibrated to the thermodynamically most stable isomer **1a**.

Nearly identical results were obtained in the reaction of C_{60} with *tert*-butyl diazo-acetate. A mixture of the [(*tert*-butoxy)carbonyl]methylene-bridged fullerenes **1b–3b** was isolated in the approximate relative intensity ratio of 1:1:3, respectively (*Fig. 3a*), which was subsequently equilibrated to give **1b** as the only compound (*Fig. 3b*). With the exception of the ester resonances, the corresponding ^{1}H- and ^{13}C-NMR spectra in both series **1a–3a** and **1b–3b** are nearly identical, and the following analysis of the spectral data for the (ethoxycarbonyl)methylene-bridged derivatives holds also for the [(*tert*-butoxy)-carbonyl]methylene analogues.
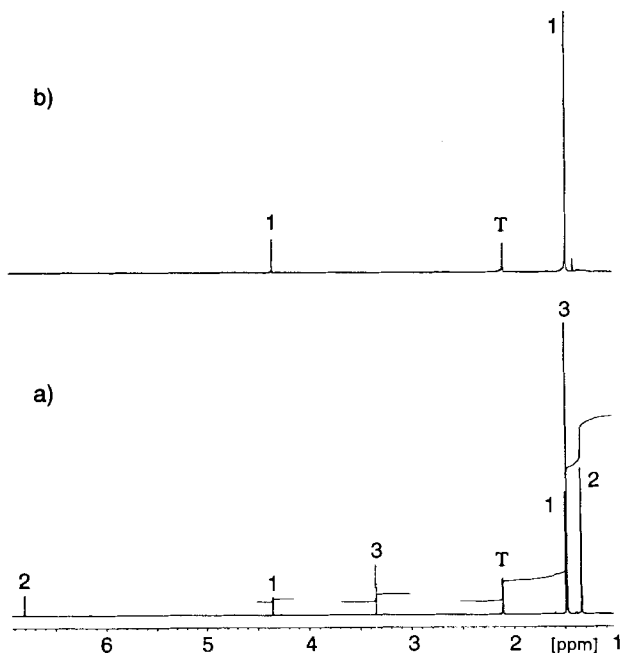

Fig. 3. *500-MHz ^{1}H-NMR Spectra recorded in C_6D_6 of* a) *the mixture of [(tert-butoxy)carbonyl]methylene-bridged fullerenes* **1b**, **2b**, *and* **3b** *in the approximate ratio of 1:1:3 and* b) *pure isomer* **1b**. T = Toluene.

The three isomers **1a–3a** differ by the position of the bridging, which occurs at the 6-6 ring junction in **1a** and at the 6-5 ring junction in **2a** and **3a**. All three structures posses C_s symmetry, and the ^{13}C-NMR spectrum of each isomer should show 32 fullerene resonances, 28 of relative intensity 2 and 4 of relative intensity 1. In agreement with this symmetry consideration, the spectrum of pure **1a** shows 32 and the spectrum of the mixture of **1a–3a** 96 fullerene resonances, respectively (*Fig. 4*). A literature survey of fullerene monoadducts with clearly defined solution or solid-state structures [10–15] [18] showed that, with the exception of the parent methano-bridged fullerene $C_{61}H_2$ [16], all monoadditions to C_{60} had occurred at the 6-6 ring junction. Apparently, bridging at the

6-6 ring junction gives the thermodynamically most stable products and, therefore, we assigned such a structure to **1a**, the only product resulting from thermal equilibration of the initial isomer mixture.

It is quite remarkable that the 96 fullerene resonances could be identified in the ^{13}C-NMR spectra of both mixtures **1a–3a** and **1b–3b** (*Figs. 4* and *5*). Expectedly, corresponding resonances of the ethoxycarbonyl and the (*tert*-butoxy)carbonyl isomers appear at nearly identical positions. In the narrow chemical-shift range between 142.00 and 146.00 ppm, as many as 68 resonances are observed in each spectrum. Only 15 overlaps of peaks occurred in the spectra of each mixture which were, however, clearly recognizable based on peak shapes and signal intensities.

The assignment of the bridging position in isomers **2a** and **3a** (as well as in **2b**/**3b**) was facilitated by a paper of *Wudl* and coworkers on the parent methano-bridged fullerene $C_{61}H_2$ (**4**) which appeared during the course of this work [16]. In **4**, bridging occurs at the 6-5 ring junction which locates one of the two CH_2 protons above a pentagon and the other one above a hexagon of the fullerene surface. As a result of the two very different environments in terms of local and ring-current anistropy effects, the chemical shifts of the two protons differ dramatically with one resonance appearing at $\delta = 2.87$ and the other at $\delta = 6.35$ (*Table 1*). Impressive similarities in the ^{1}H-NMR spectra (*Table 1*) clearly justify the assignment of structures to **2a** and **3a** in which, similar to **4**, bridging also occurs at the 6-5 ring junction. In **2a** and **3a**, the methine protons take nearly identical positions over the fullerene surface to those taken by the CH_2 protons in **4**.

Table 1. ^{13}C-NMR Chemical Shifts [ppm] for the Bridgehead C-Atoms, $^1J(C,H)$ Coupling Constants [Hz] at the Bridging C-Atom, ^{1}H-NMR Chemical Shifts [ppm] of the Protons at the Bridging C-Atom, and Bridged Ring Junction in Methano-Bridged Fullerenes

Compound	δ(Bridgehead C)	^1J(C,H at bridging C)	δ(H at bridging C)	Bridged ring junction	Homo-aromaticity
1a	71.54	166.1	4.31	6-6	σ
1b	71.74	166.7	4.38	6-6	σ
2a	> 130	143.6	6.79	6-5	π
2b	> 130	144.1	6.80	6-5	π
3a	> 130	143.0	3.32	6-5	π
3b	> 130	142.7	3.35	6-5	π
4[a]	> 130	145.0, 147.8	2.87, 6.35	6-5	π
5a[b]	78.25, 79.23	–	–	6-6	σ
5b[b]	77.05, 79.84	–	–	6-6	σ
6[c]	[d]	140	[d]	6-6	π

[a]) From [16].   [b]) From [12].   [c]) From [11].   [d]) Not reported.

Consequently, the chemical shifts of the two methine protons of **2a** and **3a** (δ 3.32 and 6.79, respectively, *Table 1*) differ equally dramatically ($\Delta\delta = 3.47$ ppm) than those of the CH_2 protons in **4** ($\Delta\delta = 3.48$ ppm). The local and ring-current anisotropy effects encountered by the methine protons in **2a** and **3a** and by the corresponding CH_2 protons in **4** are nearly identical, since the 0.44 and 0.45 ppm downfield shifts of the methine resonances in **2a** and **3a**, compared to **4**, can be fully accounted for by the β-effect (0.43 ppm) of the neighboring ester functionality [20].
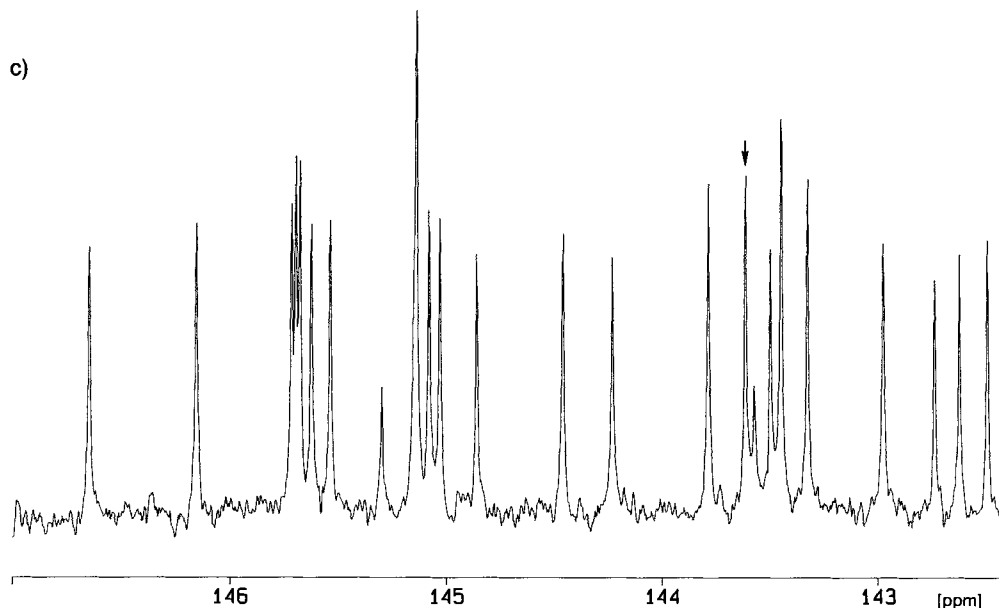
a)

Fig. 4a

b)

Fig. 4b

c)
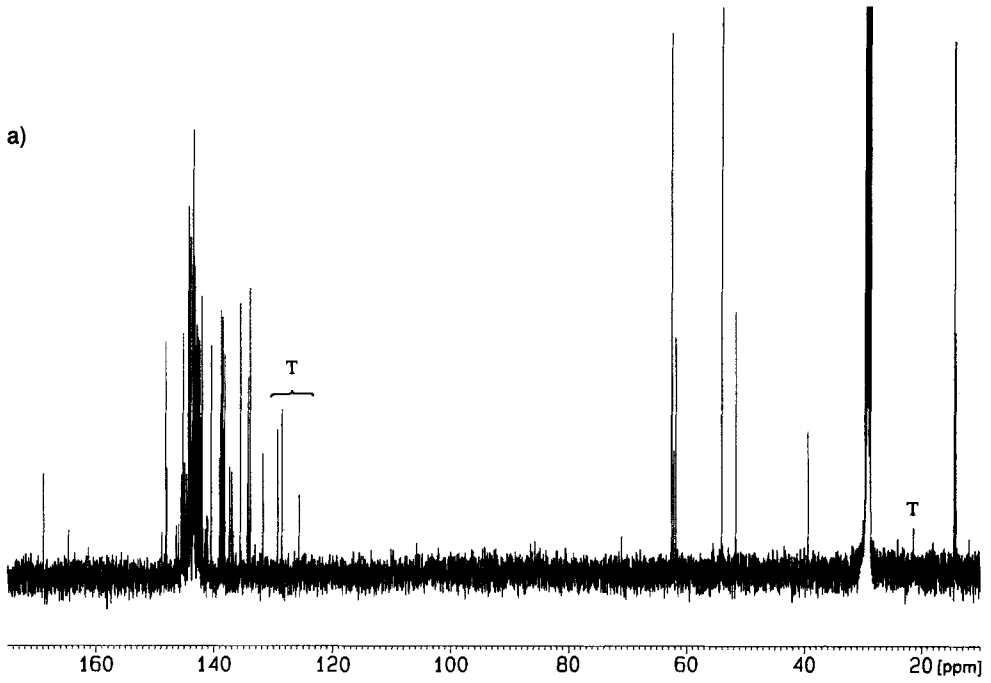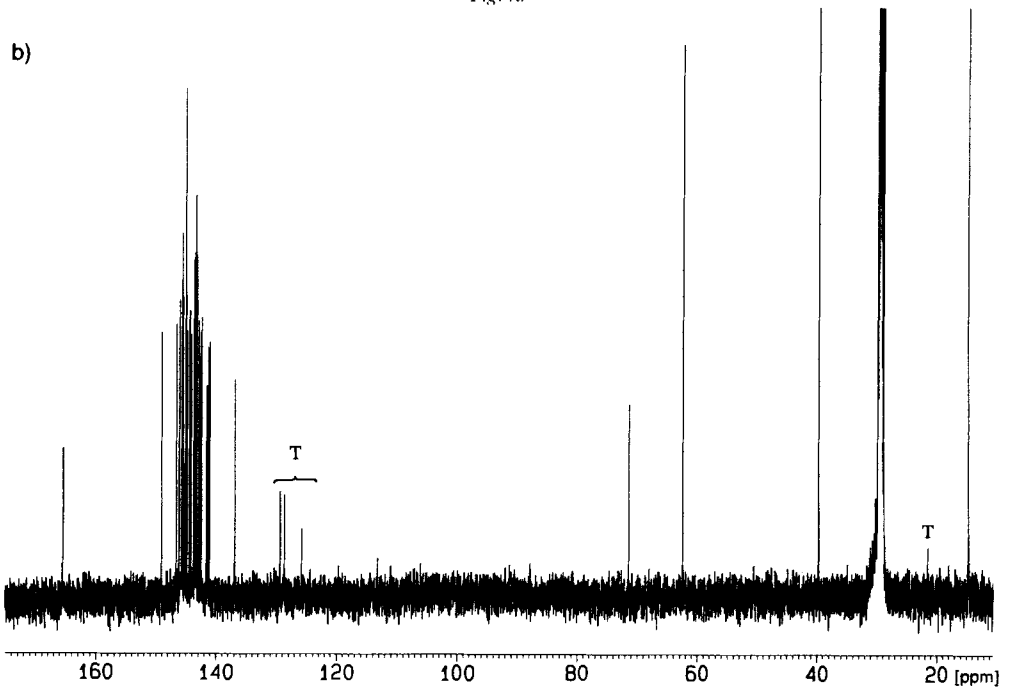
Fig. 4. *125.6-MHz ^{13}C-NMR Spectra recorded in CS_2 with (D_6)acetone as internal lock of* a) *the mixture of (ethoxycarbonyl)methylene-bridged fullerenes* **1a, 2a,** *and* **3a,** b) *pure isomer* **1a,** *and* c) *the expanded 142–147-ppm region in the spectrum of pure* **1a.** The acetone resonances appear at 29.7 and 204.0 ppm and the solvent peak at 193.0. The arrow marks the resonance at 143.43 originating from a minor C_{60} impurity in the sample. T = Toluene.

Our assignment of the downfield-shifted *singlet* at δ 6.79 (*Fig. 2a*) to the methine proton in **2a** and of the *singlet* at δ 3.32 to the methine proton in **3a** is based on a correlation between chemical shift and structure. Although the orientations of the methine protons above hexagons in **1a** and **3a** may differ slightly, the chemical shifts of these protons should be closer in value than those of methine protons located in very different environments, such as above a fullerene hexagon in **1a** and above a pentagon in **2a**. Based on this assumption, we assign the methine resonance that appears only 0.99 ppm upfield from the methine signal of **1a** to isomer **3a** and the methine resonance 2.68 ppm downfield from the methine signal of **1a** to isomer **2a**.

Recent calculations of local ring currents in C_{60} within the *London* approximation by *Pasquarello et al.* [21] could provide additional support for our assignment of the methine signals to **2a** and **3a**. These calculations predict the existence of strong local paramagnetic ring currents in the pentagons, whereas the hexagons are affected by the weaker diamagnetic ring currents that flow all around the C_{60} molecule. As a consequence, protons located closely above the center of the pentagons in C_{60} should be strongly deshielded, whereas protons above the centers of the hexagons become weakly shielded. Although this ring-current model has been derived for C_{60} only, it could also hold for **2a** and **3a** which, in contrast to **1a**, exist as methanoannulene-type structures with an 'open' transannular bond. The analysis of the electronic absorption spectra (*Fig. 6*, see below) suggests that the bridge in the 'open' structures **2a** and **3a** apparently represents only a minor perturbation of the spherical π system in C_{60}.
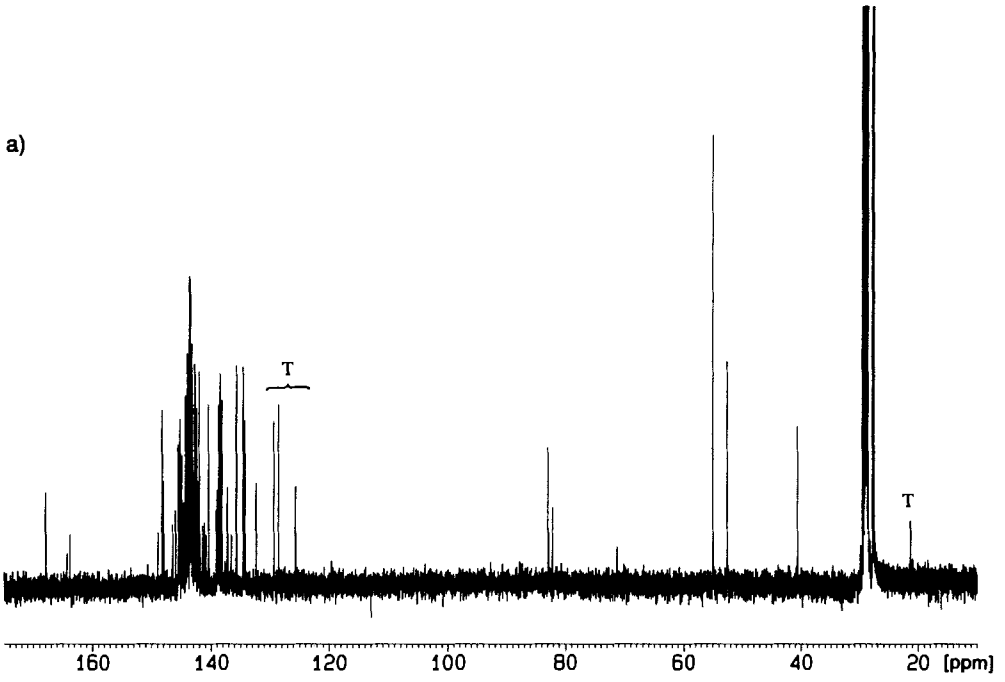
a)

Fig. 5a

b)
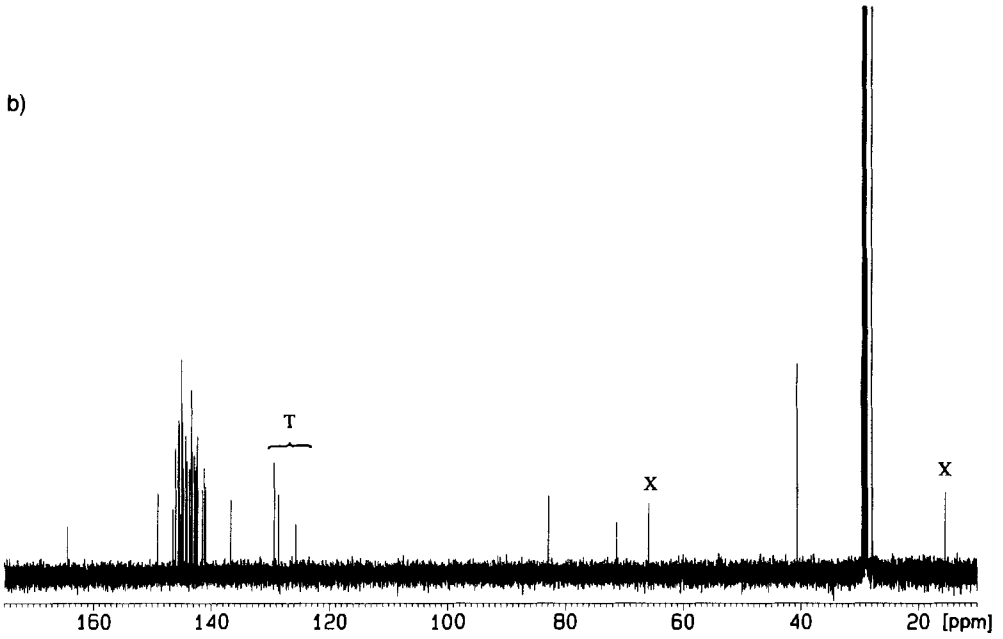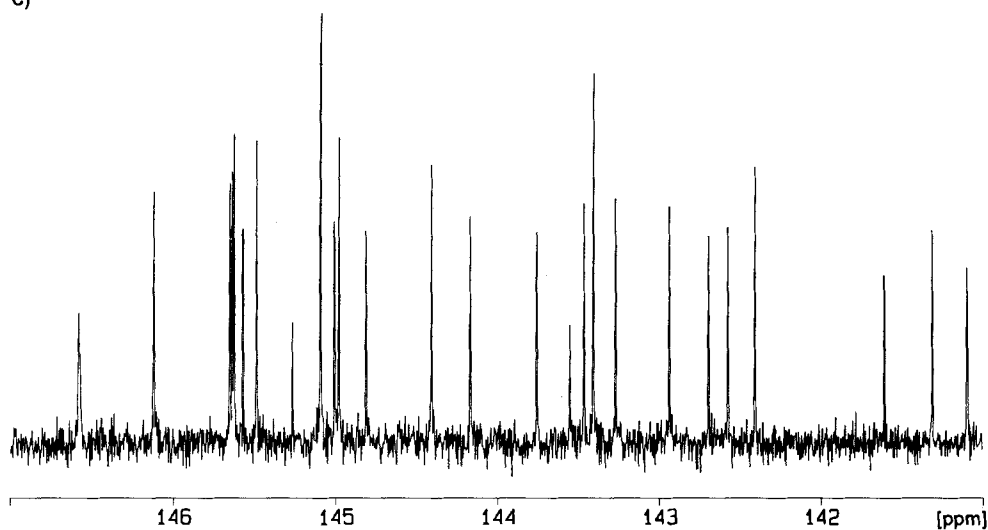
Fig. 5b

c)


Fig. 5. *125.6-MHz* ¹³*C-NMR Spectra recorded in CS$_2$ with (D$_6$)acetone as internal lock of* a) *the mixture of [(tert-butoxy)carbonyl]methylene-bridged fullerenes* **1b**, **2b**, *and* **3b**, b) *pure isomer* **1b**, *and* c) *the expanded 141–147-ppm region in the spectrum of pure* **1b**. The acetone resonances appear at 29.7 and 204.0 ppm and the solvent peak at 193.0. X in spectrum *b*): Et$_2$O. T = Toluene.

4

5a R = Bn
5b R = Piv

6 R = Ph, R' = H
7 R = R' = *p*-Br-Ph
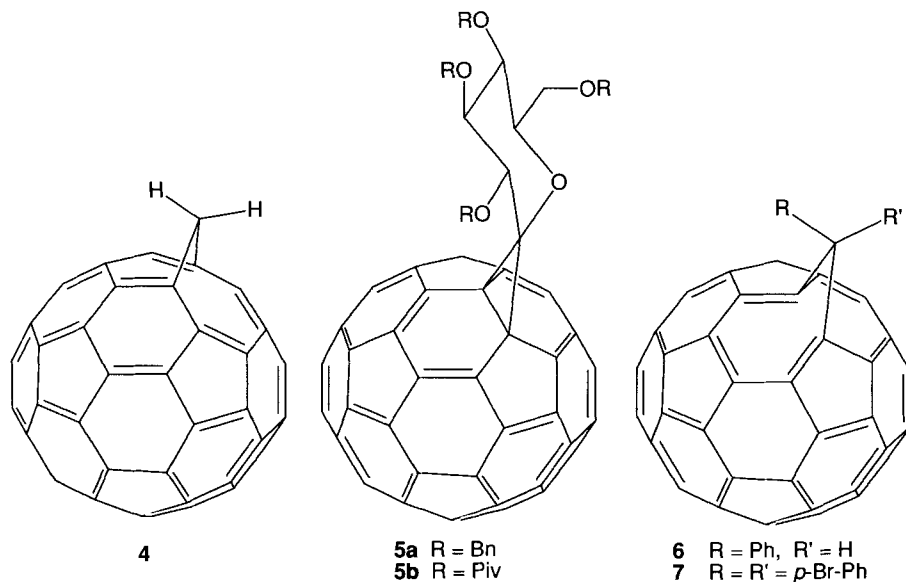
4. The Structural Linkage between Methano-Bridged Annulenes and Methano-Bridged Fullerenes. – A central question in the rich chemistry of 1,6-methano[10]-annulene (**8**) and a variety of other bridged annulenes, which was discovered and largely developed over the past three decades by *Vogel* and coworkers [22], is the extent to which the central 1,6-bond is 'open', *i.e.* whether the valence isomerization equilibrium in *Scheme 2* lies on the side of the 1,6-methano[10]annulene (π-homonaphthalene), of the olefinic 'bisnorcaradiene' (σ-homonaphthalene) [23] or somewhere between these extremes [23d].

Scheme 2

σ-**Homoaromatic** π-**Homoaromatic**
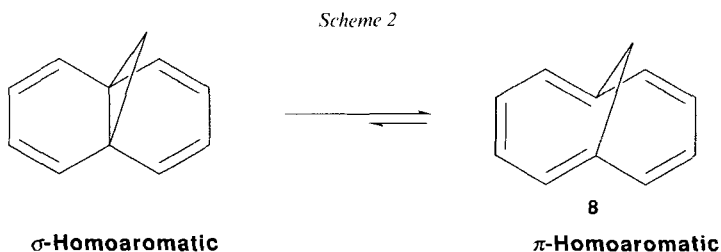
Experimentally, ^{13}C-NMR spectroscopy provides *two* strong criteria to differentiate between π-homoaromatic and σ-homoaromatic structures in methano-bridged annulenes [23]. First, the ^{13}C-NMR chemical shift is a very sensitive indicator of σ/π-homoconjugative effects. When the transannular bond is 'closed' as in **13–15**, the resonances of the bridgehead C-atoms appear at relatively high field ($\approx$ 40–60 ppm), whereas the resonances in **8** and **10–12** with an 'open' transannular bond are shifted downfield into the aromatic/olefinic region of the spectrum ($\approx$ 110–120 ppm; *Table 2*). The second NMR
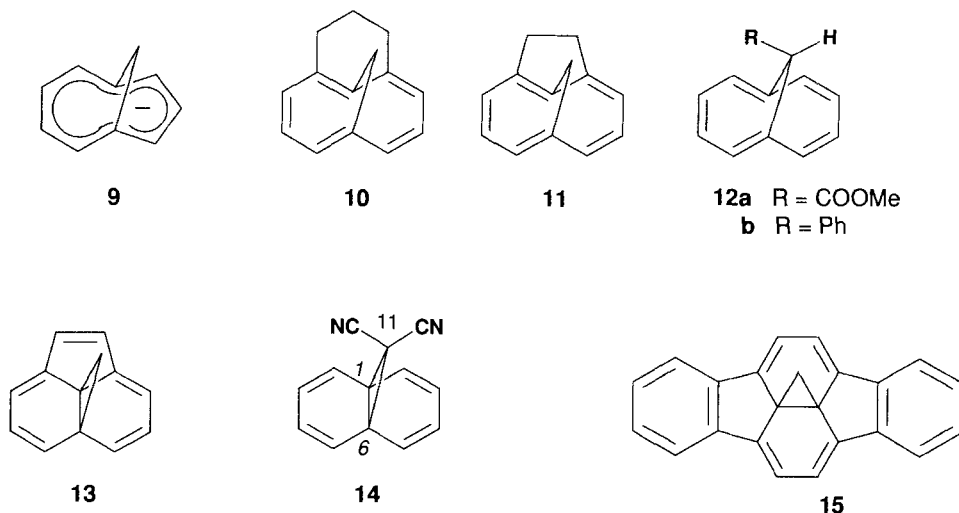

9   10   11   12a R = COOMe
                                       b   R = Ph

13   14   15

Table 2. ^{13}C-NMR Chemical Shifts [ppm] for C-Atoms C(1), C(6), $^1J(C,H)$ Coupling Constants [Hz] at C(11), ^1H-NMR Chemical Shifts [ppm] of the Bridge Protons $H-C(11)$, and Preferred Type of Homoaromaticity in Methanoannulenes

Compound	δ(C(1), C(6)) [ppm]	^1J(C(11),H–C(11)) [Hz]	δ(H–C(11)) [ppm]	Homo- aromaticity	Reference	
8	114.9	142.3	−0.45	π	[23e]	[26]
9	[a])	[a])	−1.2, −0.7	π	[27]	
10	117.17, 114.32	141.5	−0.42	π	[23e]	
11	115.41, 109.53	146.2	0.36	π	[23e]	
12a	115.43	134.5	0.49	π	[25]	[28]
12b	117.40	138	0.89	π	[25]	
13	51.14, 39.58	167.3	0.94	σ	[23e]	
14	54.46[b])	–	–	σ	[23c]	
15	59.08	169	2.55	σ	[22e]	[25]

[a]) Not reported.   [b]) At −40°.

quantity for probing the valence tautomerism in methanoannulenes has been the ^1J(C,H) coupling constant for the proton on the bridging C-atom. In the π-homoaromatic methanoannulenes **8** and **10–12**, these coupling constants typically show values around 140–145 Hz. In contrast, the σ-homoaromatic systems **13** and **15** with a 'closed' transannular bond give ^1J(C,H) coupling constants between 165 and 170 Hz. The π-homoconjugative stabilization of **8**, **10**, and **11** and the σ-homoconjugative stabilization of **13** have recently been further supported by a combined thermochemical force-field computational study [24]. As expected for a σ-homonaphthalene structure, a short transannular bond of 1.55 Å was found in the X-ray crystal structure of dibenzohomopyracylene (**15**) [22e] [25], an appropriate structural model for a C_{60} molecule with a methano bridge at the 6-6 ring junction.

The same experimental criteria – ^{13}C-NMR chemical shifts of the bridgehead C-atoms and the coupling constant ^1J(C,H) at the methano bridge C-atom – which are used to probe the bonding situation in terms of π- vs. σ-homoaromaticity in the methanoannulenes, are also applicable to address this question in the methano-bridged fullerenes [10a] [11] [16]. In isomer **1a**, the bridged fullerene C-atoms resonate at δ 71.54, in agreement with a 'closed' transannular bond (*Table 1*). Besides **1a** and **1b**, the fullerene sugars **5a/b** also prefer σ-homoconjugative stabilization, and the resonances of their bridged fullerene C-atoms appear near 79 ppm (*Table 1*). Although the chemical shifts between 70 and 80 ppm for the bridgehead atoms in **1a/b** and **5a/b** appear rather downfield from the corresponding shifts in σ-homoaromatic methanoannulenes ($\approx$ 40–60 ppm, *Table 2*), the assignment of a 'closed' transannular bond is further supported by the chemical shifts measured for these C-atoms in fullerenes fused at the 6-6 ring junction to four-membered rings (78.75 ppm) [29] and six-membered rings (66.3 and 66.09 ppm) [13a,b], which cannot undergo valence isomerization. The downfield shifts of the bridgehead C-atoms in **1a/b** and **5a/b**, compared to **13–15**, presumably originate from anisotropy and ring-current effects of the fullerene sphere.

A look at the ^{13}C-NMR spectra of the mixtures of **1a–3a** and **1b–3b** (*Figs. 4a* and *5a*) rapidly shows that the regions between 50 and 100 ppm in both spectra do not contain

more resonances than those expected for the (alkoxycarbonyl)methylene signals of three isomers in addition to one single fullerene resonance, which belongs to the bridgehead C-atoms in **1a** and **1b**. Rather, the resonances of the bridgehead atoms in **2a/b** and **3a/b** appear together with the other fullerene resonances in the typical fullerene range between 130 and 150 ppm. We take this as a very strong argument for assigning π-homoconjugated structures with 'open' transannular bonds to these isomers. Similarly, *Wudl* and coworkers found that the bridgehead C-atoms in **4** resonate between 135 and 150 ppm which also led them to assign π-homoaromaticity to the parent methano-bridged fullerene [16]. In the methanoannulene family, the π-homoaromatic 1,5-methano-[9]annulenyl anion (**9**) [27] is the structural counterpart to the 6-5-ring-bridged fullerenes **2a/b**, **3a/b**, and **4**. The downfield shift of the bridgehead C-resonances (130–150 ppm) in the π-homoaromatic methanofullerenes **1–4**, compared to the corresponding resonances in the π-homoaromatic annulenes **8** and **10–12** (110–120 ppm), can again be explained by specific influences of the fullerene sphere on the chemical shifts.

As the second probe for the valence tautomerism, we evaluated the $^1J(C,H)$ coupling constants at the methano bridge C-atoms from the ^{13}C-satellites in the 500-MHz ^{1}H-NMR spectra. For **1a** and **1b**, we measured $^1J(C,H) = 166.1$ and 166.7 Hz (*Table 1*), values expected from the methanoannulene data in *Table 2* for σ-homoaromatic structures. In contrast, the 'open' derivatives **2a/b** and **3a/b** give $^1J(C,H)$ values around 143 Hz which nearly perfectly match the data for 1,6-methano[10]-annulene (**8**). Similarly, *Wudl* and coworkers had measured $^1J(C,H) = 145.0$ and 147.8 for the two coupling constants in $C_{61}H_2$ (**4**) and 140 Hz for the phenylmethylene-bridged derivative **6**, a π-homoaromatic system like its methanoannulene counterpart **12b**. The bis(4-bromophenyl)methylene-bridged fullerene **7** also prefers the π-homonaphthalene structure; its X-ray crystallographic analysis shows a rather short transannular distance of 1.84 Å which presumably is indicative of a particularly strong homoconjugative interaction.

The electronic absorption spectra of the π-homoaromatic 6-5-ring-bridged isomers **2a/b** and **3a/b** and those of the σ-homoaromatic 6-6-ring-bridged structures **1a/b** are remarkably different. The spectra of the pink-red isomers **1a** and **1b** (*Fig. 6*) closely resemble those measured for the wine-red colored fullerene sugars **5a** and **5b**. Compared to the spectrum of C_{60}, the long-wavelength absorption between λ 450 and 700 nm is much less structured, and its maximum is hypsochromically shifted to near 500 nm. New in the spectra of **1a/b** and **5a/b** is a sharp band with λ_{max} near 430 nm. This band seems to be highly characteristic for 'closed' 6-6 ring-bridged fullerenes. Not only does this characteristic sharp absorption band appear in the spectra of the σ-homoaromatic structures **1a/b** ($\lambda_{max} = 429$ nm) and **5a/b** ($\lambda_{max} = 433$ and 432 nm, respectively), but it is also present in the spectrum of a fullerene bridged at the closed 6-6 ring junction by a six-membered ring ($\lambda_{max} = 435$ nm) [13a] as well as in the spectrum of $C_{60}O$ with the O-atom bridging the 6-6 ring junction ($\lambda_{max} = 424$ nm) [18a]. The origin of this interesting electronic transition remains to be addressed.

In contrast to the spectra recorded for **1a/b** and **5a/b**, those of the purple mixtures of **1a–3a** and **1b–3b**, which contain a $\sim 4:1$ ratio of 'open' 6-5-ring-bridged to 'closed' 6-6-ring-bridged isomers, resemble much more the spectrum of C_{60} itself (*Fig. 6*). Similarly, *Wudl* and coworkers reported that the UV/VIS spectrum of purple-colored **4** is virtually identical to the spectrum of buckminsterfullerene [16]. Clearly, in the 'open'
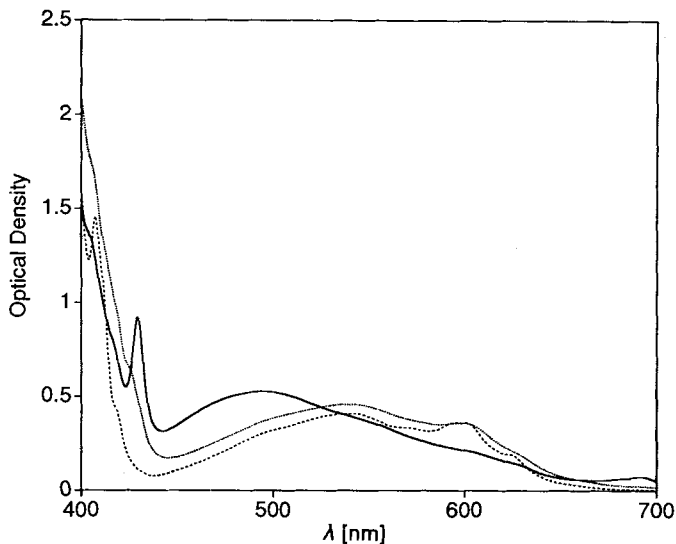
Fig. 6. *Electronic-absorption spectra recorded in toluene* ($T = 293$ K, $d = 1$ cm) *of the mixture of (ethoxy-carbonyl)methylene-bridged fullerenes* **1a–3a** *with the relative intensity ratio* 1:1:3 (· · · · ·, *c* undetermined), *of pure isomer* **1a** (——, $c = 4.13 \times 10^{-4}$ mol l^{-1}), *and of* C_{60} (-----, $c = 5.11 \times 10^{-4}$ mol l^{-1})

6-5-ring-bridged form, the spherical chromophore of the pure fullerene is less perturbed than in the 'closed' 6-6-ring-bridged form.

The question of 'open' *vs.* 'closed' transannular bond has also been raised in the structural analysis of the fullerene oxide C_{2v}-C_{60}O with the O-atom bridging the 6-6-ring junction [17] [18]. The ^{13}C-NMR resonance of the bridged C-atoms was observed at 90.18 ppm, which is indicative of an epoxide geometry. In contrast, 1,6-oxido[10]annulene prefers the π-homoaromatic structure, and the bridgehead ^{13}C resonances appear between 124 and 131 ppm. Interestingly, a recent computational study by *Raghavachari* predicts that the isomeric C_s-C_{60}O with the O-atom bridging at the 6-5-ring junction should not only be more stable than the already isolated C_{2v}-C_{60}O isomer, but that the C_s-isomer exists in the 'open' oxidoannulene form and not as the epoxide [30].

5. Preliminary Mechanistic Observations. – Although the present study provides convincing structural assignments, facilitated by the previous work on methanoannulenes, many other questions remain wide open. Why do **1–3** form reproducibly in the approximate ratio of 1:1:3, a ratio already observed in ^{1}H-NMR spectra recorded within the first hour of the reaction? The molecule C_{60} contains 90 bonds of which 60 are at 6-5 ring junctions and 30 at 6-6 ring junctions. Hence, for a totally nondiscriminating reagent, an initial product ratio of 1:1:1 would be expected; however, we find clear preference for the kinetic attack at the 6-5 ring junction. Moreover, structures **3a/b** predominate over **2a/b** by a ratio of 3:1. This represents a sizable diastereoselectivity for a molecule that has no discernible steric effect. The entirety of this selectivity must arise from electronic effects, and computational studies are under way to explain this selectivity [31].

There may be more than one mechanism leading from diazo compounds and C_{60} to methanofullerenes. Both 1,3-dipolar cycloaddition followed by rapid loss of N_2 as well as thermal decomposition of the diazo compound followed by addition of the formed carbene could explain the formation of the observed products. Although we did not obtain any evidence for the formation of pyrazoline intermediates, the 1,3-dipolar cyclo-addition, soundly established by the work of *Wudl* and coworkers in the formation of **4** [16], followed by rapid N_2 loss at the temperature of refluxing toluene cannot be excluded. Both mechanisms could actually occur concurrently under our reaction conditions, and more work is required to define the conditions under which a true carbene attack occurs. The formation of the fullerene sugars by reaction of C_{60} with nucleophilic glycosylidene carbenes provides today the best example for a possible carbene attack [12]. Different mechanisms may also be responsible for the observed selectivity of kinetic attack.

How does the isomerization to the thermodynamically stable isomer proceed? The conceptually most simple mechanism involves a [1,5] shift of the methano bridge in isomers **2** and **3** [16] [23e] [32]. Another possibility would include *retro*-carbene additions coupled to additions, until the reagent adds to the right bond. We have preliminary evidence that the isomerization mechanism may not be a simple [1,5] shift and probably involves intermolecular reactions. The best procedure for making *pure* **1a/b** is heating C_{60} and the diazoacetate to reflux for 7 h, working up the reaction, and refluxing the isolated isomeric mixture for 24 h. When C_{60} and the alkyl diazoacetates are reacted in refluxing toluene for 31 h, without isolation of the isomers after 7 h, thermal equilibration is far from completion, and the product isolated by chromatography is still a mixture of isomers, such as **1a–3a**, in the ratio of *ca.* 4:1:4. This reproducible finding, which awaits further study and explanation, may suggest that the isomerization mechanism is not a simple [1,5] shift but probably involves intermolecular reactions.

6. Conclusions. – This paper describes a rapid, inexpensive method for purification of C_{60} by simple filtration of the fullerene soot extract through a short plug of charcoal/silica gel with toluene as the eluent. Reactions of C_{60} with ethyl and *tert*-butyl diazoacetates in refluxing toluene initially lead to the formation of three (alkoxycarbonyl)methylene-bridged isomers **1a–3a** and **1b–3b**, respectively, which can be equilibrated upon further heating into the single compounds **1a** and **1b**, respectively. The analysis of the ^{1}H-NMR chemical shifts and the number of ^{13}C-NMR resonances shows that the bridges in **1a/b** are located at the 6-6 ring junction, whereas structures **2a/b** and **3a/b** are bridged at the 6-5 ring junction. Based on dramatic influences of local and π-ring-current anisotropic effects on ^{1}H-NMR chemical shifts and on theoretical calculations, the methine proton is proposed to be located over the pentagon ring in **2a/b** and over the hexagon in **3a/b**. With the help of two independent NMR criteria, the ^{13}C-NMR chemical shift of the bridgehead C-atoms and the coupling constant $^1J(C,H)$ at the methano bridge, a π-homoaromatic structure with an 'open' transannular bond is assigned to isomers **2a/b** and **3a/b** and a σ-homoaromatic structure with a 'closed' transannular bond to **1a/b**. This analysis had previously been developed to clarify the preference for π- or σ-homoconjugation in methanoannulenes. We believe that the results described in this paper fully justify the statement recently made by *Vogel* about the 'fascinating linkage between the chemistry of 1,6-bridged [10]annulene and buckminsterfullerene' [22e] and, therefore, propose to

name the methylene-bridged fullerenes as *methanofullerenes* to indicate the close structural analogy to the methanoannulenes.

Many questions remain unanswered. It is not yet clear whether electronic or steric factors or both are at the origin of the preference for π-homoconjugation at the 6-5 ring junction and σ-homoconjugation at the 6-6 ring junction. Do both the carbene addition and the 1,3-dipolar cycloaddition, followed by N_2 extrusion, produce methano-bridged fullerenes, and what are the experimental conditions which lead to preference of one of the two mechanisms? What is the mechanism of the isomer equilibration? Do substituents at the methano bridge affect the valence isomerization in methanofullerenes in a similar way to the effects established for the cycloheptatriene-norcaradiene tautomerization [22b] [24] [33]? We hope to answer some of these fundamental questions in the continuation of this work.

Experimental Part

General. Reagents used were reagent-grade commercials. *tert*-Butyl diazoacetate was prepared according to [34]. The crude fullerene-enriched soot, containing *ca.* 5% soluble fullerenes, was purchased from *Polygon Enterprises*, P. O. Box 5536, Waco, USA, and *Texas Fullerene Corporation*, 8926 Kirby Drive, Houston, USA. Fullerene soot extract was obtained by *Soxhlet* extraction of the fullerene-enriched soot with toluene. Silica gel (230–400 mesh, 0.040–0.063 mm) for C_{60} purification was from *E. Merck*. Charcoal was *Fluka* activated, acid-washed charcoal *Darco G60*. Column chromatography of the bridged fullerenes was performed on silica gel 70–230 mesh from *E. Merck*. HPLC Analysis [5b] [35] was carried out on a *Vydac 201 TP* C_{18} reversed-phase column using toluene/MeCN 1:1 (*v/v*) as eluent with 310-nm UV detection. The *Vydac* column was purchased from *The Separations Group*, 17434 Mojave St., Hesperia, CA 92345, USA, also from *Paul Bucher*, Schützengraben 7, CH–4051 Basel. UV/VIS Spectra were recorded on a *CARY 5* spectrometer. 400- and 500-MHz ^{1}H- and 125.6-MHz ^{13}C-NMR spectra were measured at 293 K if not stated otherwise. Fast-atom-bombardment spectra (FAB-MS) were determined in *m*-nitrobenzyl alcohol as the matrix. Elemental analyses were effected by the Mikrolabor in the Laboratorium für Organische Chemie at ETHZ.

Purification of C_{60}. A slurry of 125 g of silica gel (230–400 mesh) and 63 g *Darco G60* charcoal in 800 ml of toluene was shaken for 5 min until homogeneous. This slurry was loaded onto a glass filter funnel with a *D4* frit (diameter 10 cm) mounted on a suction flask to give a plug of 5.5-cm height. The plug must not be allowed to become solvent-free, or else cracking of the stationary phase can occur. The plug is covered with 1 cm of washed sea sand and loaded with a highly conc. soln. of 2.54 g of fullerene soot extract. The loading of the plug as well as the separation take place at low vacuum (*ca.* 50 Torr) applied to the suction flask. The plug is rinsed with 3.5 l of toluene whereby the filtrate turns intensively purple after elution with 300 ml of solvent. The complete separation takes *ca.* 15 min. The deep-colored soln. is concentrated to dryness and the residue washed on a *D4* frit with small portions of Et_2O [7] to give 1.50 g of C_{60} (60% of a possible 75% present in the fullerene soot extract). HPLC Analysis showed only C_{60} with no detection of C_{70} or any of the higher fullerenes. Depending on the amount of fullerene oxides present in the crude fullerene soot, the purified C_{60} contains 1–3% of $C_{60}O$.

For the preparation of highest-purity C_{60}, a glass filter funnel with a *D4* frit (diameter 6.5 cm) on a suction flask is filled with a slurry of 84 g of silica gel (230–400 mesh) and 42 g of charcoal *Darco G60* in toluene to give a plug of 9-cm height. The plug is covered with 1 cm of sea sand and loaded with a highly conc. soln. of 1.70 g of fullerene soot extract in 500 ml of toluene. The plug is rinsed with 2.6 l of toluene. The first fraction of 1.4 l of deep

purple soln. is concentrated to dryness and the residue washed on a *D4* frit with small portions of Et_2O to give 693 mg (41% of a possible 75% C_{60} in the fullerene soot extract) of C_{60}. HPLC Analysis shows C_{60} in a purity of 99.75%. The second fraction of 1.2 l gives, after concentration and washing with Et_2O, additional 143 mg (14%) of C_{60} of 99.2% purity containing 0.8% of $C_{60}O$ as the only side product.

(Ethoxycarbonyl)methylene-Bridged C_{60} Isomer **1a**. To a soln. of 105 mg (0.146 mmol) of C_{60} in 105 ml of toluene was added 16.6 mg (0.146 mmol) of ethyl diazoacetate in 1 ml of toluene. The mixture was heated to reflux for 7 h during which time the color turned from purple to wine-red. To the cooled soln. was added a portion of silica gel (30 g), and the solvent was evaporated under reduced pressure. The resulting solid was added on top of a silica-gel column which was first eluted with hexanes to remove residual C_{60}, then with toluene/hexanes 1:1 (v/v). The major product fraction eluting with R_f 0.43 in the binary solvent mixture was isolated and characterized to be 35 mg (30%) a 1:1:3 mixture of isomers **1a–3a**. UV/VIS (λ_{max} (ε) in toluene): 597, 539 (br.), 425 (sh), 406 (sh), 337. IR (KBr): 1741s, 1426w, 1183m, 1154m, 1019w, 577w, 526s. ¹H-NMR (400 MHz, C_6D_6): **1a**: see spectrum listed for pure compound below; **2a**: 6.79 (s, 1 H); 3.90 (q, J = 7.1, 2 H); 0.92 (t, J = 7.1, 3 H); **3a**: 4.17 (q, J = 7.1, 2 H); 3.32 (s, 1 H), 1.01 (t, J = 7.1, 3 H). ¹³C-NMR (125.6 MHz, $CS_2/(D_6)$acetone 10:1, v/v): **1a**: all 36 resonances known from the spectrum of pure **1a** listed below are observed; non-fullerene resonances of **2a**: 164.78 (*C*OOEt); 62.36 (CH_3CH_2); 14.90 (CH_3CH_2); non-fullerene resonances of **3a**: 168.96 (*C*OOEt); 63.02 (CH_3CH_2); 15.08 (CH_3CH_2); 26 fullerene resonances clearly belonging to the more abundant isomer **3a**: 148.33; 144.46; 144.21; 144.13; 144.11; 143.81; 143.74; 143.69; 143.67; 143.61; 143.53; 143.51; 143.39; 143.30; 143.03; 142.89; 142.64; 142.24; 140.65; 138.96; 138.91; 138.73; 138.37; 135.77; 134.48; 134.12; 38 fullerene resonances belonging to **2a** (32) and **3a** (6): 148.13; 145.46; 145.38 (2×); 145.35; 145.34; 145.18; 145.13; 144.78; 144.46; 144.34; 144.24; 144.12; 144.11; 144.08; 143.97; 143.81; 143.73; 143.68; 143.66; 143.43; 143.38; 143.10; 142.83; 142.80; 142.49; 142.39; 142.23; 140.64; 139.23; 139.18; 138.66; 138.47; 138.46; 137.61; 137.24; 134.55; 131.96. FAB-MS: 807 (M^+); 733 ($[M - COOEt]^+$); 720 ($[M - CHCOOEt]^+$).

A soln. of 35 mg (0.043 mmol) of the mixture **1a–3a** in 105 ml of toluene was heated to reflux for 24 h during which the initially purple soln. turned to a pink-red color. Chromatography as above gave a pink-red product fraction, eluting at the same R_f value as the initial isomeric mixture, which was evaporated to dryness. After washing the resulting solid with Et_2O and drying (25° 0.1 Torr), 31 mg (89%) of **1a** was obtained as black microcrystalline material which tenaceously retains traces of residual toluene. UV/VIS (λ_{max} (ε) in toluene): 495 (br., 1250), 429 (2250), 417 (1900), 404 (sh, 3300), 395 (sh, 5250), 331 (40250). IR (KBr): 2973w, 1742s, 1427w, 1185s, 1155s, 1025m, 738w, 705w, 575m, 527s. ¹H-NMR (400 MHz, C_6D_6): 4.31 (s, 1 H); 4.10 (q, J = 7.1, 2 H); 1.06 (t, J = 7.1, 3 H). ¹³C-NMR (125.6 MHz, $CS_2/(D_6)$acetone 10:1, v/v): 165.44 (*C*OOEt); 149.07; 146.65; 146.16; 145.72; 145.70 (2×); 145.68; 145.63; 145.54; 145.30; 145.14 (2×); 145.08; 145.03; 144.86; 144.46; 144.23; 143.79; 143.58; 143.50; 143.45 (2×); 143.33; 142.98; 142.74; 142.62; 142.49; 141.63; 141.36; 141.14; 136.99; 71.59 (32 fullerene resonances); 62.70 (CH_3CH_2); 40.01 (*C*HCO_2Et); 14.99 (CH_3CH_2). The peak of a minor C_{60} impurity (*ca.* 1%) appears at 143.45 as impurity. FAB-MS: 807 (M^+); 733 ($[M - COOEt]^+$); 720 ($[M - CHCOOEt]^+$). Anal. calc. for $C_{64}H_6O_2$ (806.75): C 95.28, H 0.75, O 3.97; found: C 94.70, H 0.95, O 3.87.

[(tert-Butoxy)carbonyl]methylene-Bridged C_{60} Isomer **1b**. Following an identical procedure to that described for the conversion with ethyl diazoacetate, 69.5 mg (0.0964 mmol) of C_{60} was reacted with 13.7 mg (0.0964 mmol) of *tert*-butyl diazoacetate to give 20 mg (25%) of the isomeric mixture **1b–3b** in the approximate ratio 1:1:3. UV/VIS (λ_{max} (ε) in toluene): 627 (sh), 595, 537 (br.), 424 (sh), 413 (sh), 337. IR (KBr): 2974w, 1737m, 1638w, 1617w, 1400s, 1147m, 580w, 526m. ¹H-NMR (500 MHz, C_6D_6): **1b**: see spectrum listed for pure compound below; **2b**: 6.80 (s, 1 H); 1.34 (s, 9 H); **3b**: 3.35 (s, 1 H); 1.48 (s, 9 H); ¹³C-NMR (125.6 MHz, $CS_2/(D_6)$acetone 10:1, v/v): **1b**: all 36 resonances known from the spectrum of pure **1b** listed below are observed; non-fullerene resonances of **2b**: 163.85 (*C*OOC(CH₃)₃); 82.60 (COO*C*(CH₃)₃); 28.28 ((*C*H₃)₃C); non-fullerene resonances of **3b**: 168.00 (*C*OOC(CH₃)₃); 83.37 (COO*C*(CH₃)₃); 28.51 ((*C*H₃)₃C); 28 fullerene resonances clearly belonging to the more abundant isomer **3b**: 148.33; 144.44; 144.29; 144.16; 144.10; 144.07; 143.76; 143.72; 143.69; 143.64; 143.62; 143.58; 143.49; 143.46; 143.33; 143.28; 142.94; 142.89; 142.63; 142.19; 140.60; 138.89; 138.83; 138.66; 138.33; 135.89; 134.76; 134.47; fullerene resonances belonging to **2b** (32) and **3b** (4): 148.12; 145.44; 145.37 (2×); 145.31 (2×); 145.13; 145.11; 144.75; 144.40; 144.30; 144.21; 144.10; 144.04; 143.94; 143.76; 143.72; 143.69; 143.64; 143.58; 143.21; 143.03; 142.94; 142.79; 142.31; 142.17; 140.60; 139.26; 139.15; 138.60; 138.44; 138.42; 137.48; 137.39; 134.54; 132.57.

Following the protocol for the preparation of isomerically pure **1a**, 20 mg (0.0246 mmol) of the mixture **1b–3b** was equilibrated to give 15.0 mg (75%) of pure isomer **1b** which tenaceously retains traces of residual toluene. UV/VIS (λ_{max} (ε) in toluene): 593 (br., 750), 503 (1150), 429 (1800), 406 (sh, 3850), 334 (40950). IR (KBr): 2971w, 1733s, 1426w, 1384m, 1366m, 1141s, 577m, 526s. ¹H-NMR (500 MHz, C_6D_6): 4.38 (s, 1 H); 1.51 (s, 9 H). ¹³C-NMR

(125.6 MHz, $CS_2/(D_6)$acetone 10:1, v/v): 164.33 (CO); 149.07; 146.58; 146.12; 145.65; 145.64 (2×); 145.63; 145.57; 145.49; 145.27; 145.09 (2×); 145.01; 144.98; 144.82; 144.41; 144.17; 143.76; 143.55; 143.47; 143.41 (2×); 143.27; 142.94; 142.70; 142.58; 142.41; 141.61; 141.32; 141.10; 136.78; 71.74 (32 fullerene resonances); 83.28 ($COOC(CH_3)_3$); 41.21 ($CHCOO(CH_3)_3$); 28.58 ($CH_3)_3C$). FAB-MS: 834 (M^+), 778 ([M − isobutylene]$^+$); 733 ([M − $COO(CH_3)_3$]$^+$); 720 ([M − $CHCO_2(CH_3)_3$]$^+$).

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