Photophysical Properties of Three Methanofullerene Derivatives

René V. Bensasson,* Elisabeth Bienvenüe, Claude Fabre,† Jean-Marc Janot, Edward J. Land, Sydney Leach, Virginie Leboulaire, André Rassat,* Stéphane Roux, and Patrick Seta

Abstract: The [6,6]-ring bridged methanofullerenes 61,61-bis[4-*tert*-butylbenzoate]-1,2-dihydro-1,2-methanofullerene[60] (**1**), 61,61-bis[4-(*tert*-butyldiphenylsilyloxymethyl)phenyl]-1,2-dihydro-1,2-methanofullerene[60] (**2**), and 61-[(ethoxycarbonyl)methylcarboxylate]-1,2-dihydro-1,2-methanofullerene[60] (**3**) were synthesized by the Diederich method (**3**) or the Wudl method via tosylhydrazone salts (**1** and **2**). Ground-state absorption spectra of the methanofullerenes in toluene and cyclohexane solutions are presented and possible assignments discussed. The sharp, 430 nm transition is associated with the existence of less than 60 π electrons, whereas a broad band peaking at 495 nm as well as weak features in the 700 nm region could be related to forbidden transitions of C_{60}. The allowed transitions of C_{60} in the UV region are modified relatively little in the methanofullerenes. Laser flash photolysis and pulse radiolysis techniques were used to obtain triplet–triplet absorption spectra between 400 and 1100 nm and determine photophysical properties. The three methanofullerenes have very similar T–T spectra, with a strong peak at 720 nm whose molar absorption coefficient is of the order of $14000\,\text{M}^{-1}\,\text{cm}^{-1}$, somewhat lower than the $20200\,\text{M}^{-1}\,\text{cm}^{-1}$ measured for the corresponding 750 nm band of C_{60}. Values near unity were determined for Φ_Δ, the quantum yield for $^1O_2(^1\Delta_g)$ production by energy transfer from the triplet state of the three methanofullerenes, implying that the quantum yield of triplet production of each is ≈ 1. The results indicate that it is possible for the spectroscopic and photophysical properties of methanofullerenes to vary little with the nature of the methano adduct and to undergo only slight modifications with respect to the corresponding properties of C_{60}. Up to now, this has been found valid only when the functionalization does not involve an electron donor. The biological photosensitization efficiencies of these methanofullerenes are therefore expected to be similar to those of C_{60} but with their hydrophobicity and intracellular site delivery modulated by the nature of the methano-adduct.

Keywords: fullerenes • photochemistry • synthetic methods • triplet-state properties • UV/Vis spectroscopy

Introduction

The first synthesis of a methanofullerene[1] has been followed by other related functionalizations.[2–5] Certain such modified fullerenes have been shown to exhibit photosensitizing properties towards living cells, enzymes, viruses, and DNA, including photoinduced DNA cleavage[6] by singlet oxygen production.

To help quantify the efficiencies of such photoprocesses for modified fullerenes, we have synthesized three methanofullerenes, using Diederich[7,8] and Wudl methods,[9] and determined their spectroscopic and photophysical properties. These three methanofullerenes are: 61,61-bis[4-*tert*-butylbenzoate]-1,2-dihydro-1,2-methanofullerene[60] (**1**), 61,61-bis[4-(*tert*-butyldiphenylsilyloxymethyl)phenyl]-1,2-dihydro-1,2-methanofullerene[60] (**2**), and 61-[(ethoxycarbonyl)methylcarboxylate]-1,2-dihydro-1,2-methanofullerene[60] (**3**), the [6,6]-closed structures of which are shown here. For such molecules, bridging can occur at either [6,6]- or [6,5]-ring junctions. In [6,6] structures, an originally double bond of C_{60}

---

[*] Prof. R. V. Bensasson
Laboratoires de Biophysique et de Photobiologie
Muséum National d'Histoire Naturelle, CNRS UA481
INSERM U201, 43 rue Cuvier, F-75231 Paris Cedex 05 (France)
Fax: Int. code + (33) 140793705
e-mail: rvb@mnhn.fr

E. Bienvenüe, J.-M. Janot, P. Seta
Laboratoire des Matériaux et Procédés Membranaires
UMR 5635 du CNRS
1919 Route de Mende, F-34293 Montpellier Cedex 5 (France)

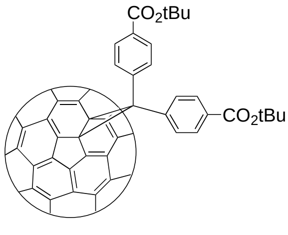
C. Fabre,[†] V. Leboulaire, A. Rassat, S. Roux
Laboratoire de Chimie, Ecole Normale Supérieure
24 rue Lhomond, F-75231 Paris Cedex 05 (France)

E. J. Land
CRC Department of Biophysical Chemistry
Paterson Institute for Cancer Research
Christie Hospital NHS Trust, Manchester M20 9BX (UK)

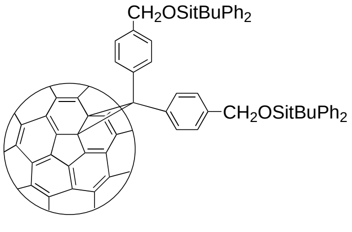
S. Leach
DAMAP, CNRS URA 812, Observatoire de Paris-Meudon
F-92195 Meudon (France)

[†] Deceased 25 March 1997.

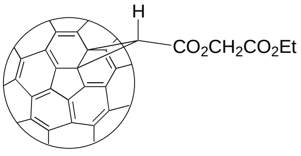
0947-6539/98/0402-0270 $ 17.50+.50/0



1



2



3

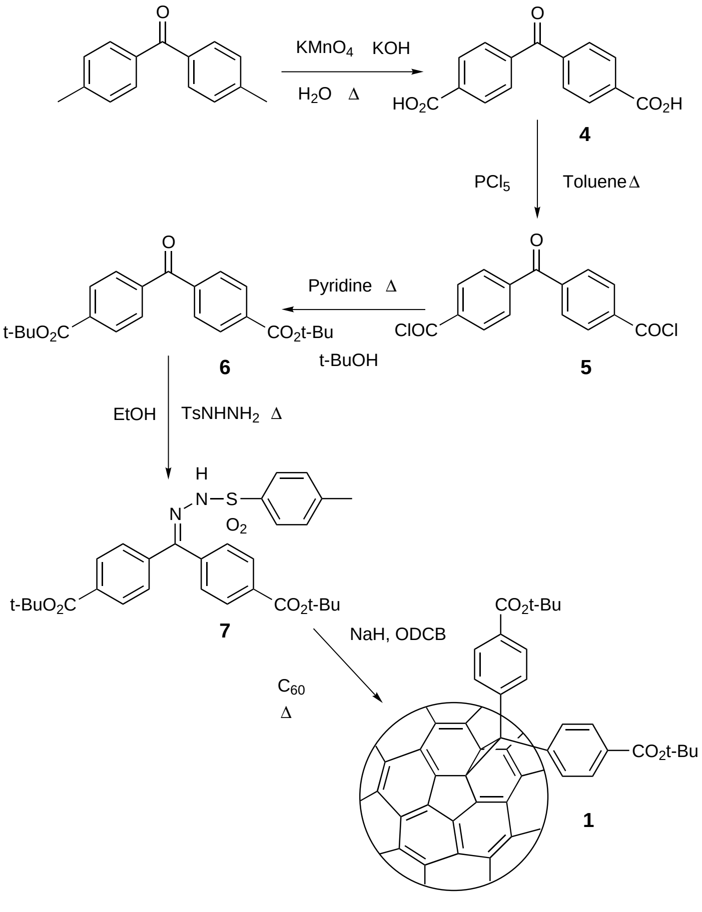
is bridged, whereas an originally single bond is bridged in [6,5] structures. The two most stable isomers are the [6,6]-closed and [6,5]-open.[2] Upon heating, the mixture of [6,6]-closed and [6,5]-open isomers formed together in the course of the synthesis are converted exclusively to the [6,6]-closed, most stable, isomer.[3,7,10]

Abstract in French: *Nous avons synthétisé par la méthode de Diederich ou de Wudl trois méthanofullerènes de type [6,6] fermé: le 61,61-bis[4-tert-butylbenzoate]-1,2-dihydro-1,2-méthanofullerène[60] (**1**), le 61,61-bis[4-(tert-butyldiphénylsilyloxyméthyl)phényl]-1,2-dihydro-1,2-méthanofullerène[60] (**2**) et le 61-[(éthoxycarbonyl)méthylcarboxylate] - 1,2-dihydro-1,2-méthanofullerène[60] (**3**). Les spectres d'absorption à l'état fondamental de ces méthanofullerènes en solution dans le toluène et le cyclohexane sont présentés et les attributions des bandes sont discutées. La bande étroite à 430 nm est associée à un défaut d'électrons π par rapport au C_{60}, tandis que la bande large centrée à 495 nm ainsi que les faibles bandes dans la région de 700 nm pourraient être dues à des transitions qui sont interdites dans le cas du C_{60}. Les transitions permises du C_{60} dans l'ultra-violet sont relativement peu modifiées dans les méthanofullerènes. Les techniques de photolyse par éclair et de radiolyse pulsée ont permis d'obtenir les spectres d'absorption de l'état triplet entre 400 et 1100 nm, caractérisés pour les trois méthanofullerènes par un coefficient molaire d'absorption de l'ordre de 14000 $\text{M}^{-1}\,cm^{-1}$ au maximum d'absorption à 720 nm, inférieur à celui du C_{60} (20200 $\text{M}^{-1}\,cm^{-1}$ au maximum d'absorption à 750 nm). Pour les trois molécules étudiées, le rendement quantique, Φ_{Δ}, de production d'oxygène singulet, $^1O_2(^1\Delta_g)$, est proche de l'unité, ce qui implique un rendement quantique de formation de l'état triplet Φ_T voisin de 1. Ces résultats indiquent que les propriétés spectroscopiques et photophysiques de nos méthanofullerènes varient peu avec la nature des substituants du pont méthano et ne présentent pas de modifications importantes par rapport au C_{60}. Ceci ne reste vrai que si la fonctionalisation n'introduit pas de donneur d'électron. Les méthanofullerènes, du type étudié dans le présent travail, devraient conserver une efficacité de photosensibilisateur proches de celle du C_{60}. Des modifications appropriées des substituants du pont méthano devraient modifier leur lipophilie et de ce fait moduler leur répartition entre différents sites intracellulaires.*

We studied the ground-state and triplet excited-state absorption spectra of the three methanofullerenes **1**, **2,** and **3**. The samples contained exclusively the [6,6]-closed isomer. Using C_{60} as reference, we determined the quantum yield for the sensitized formation of singlet oxygen, Φ_{Δ}, the triplet quantum yield of formation, Φ_{T}, and the triplet molar absorption coefficient, ε_{T}, for the three C_{61} derivatives.

Results and Discussion

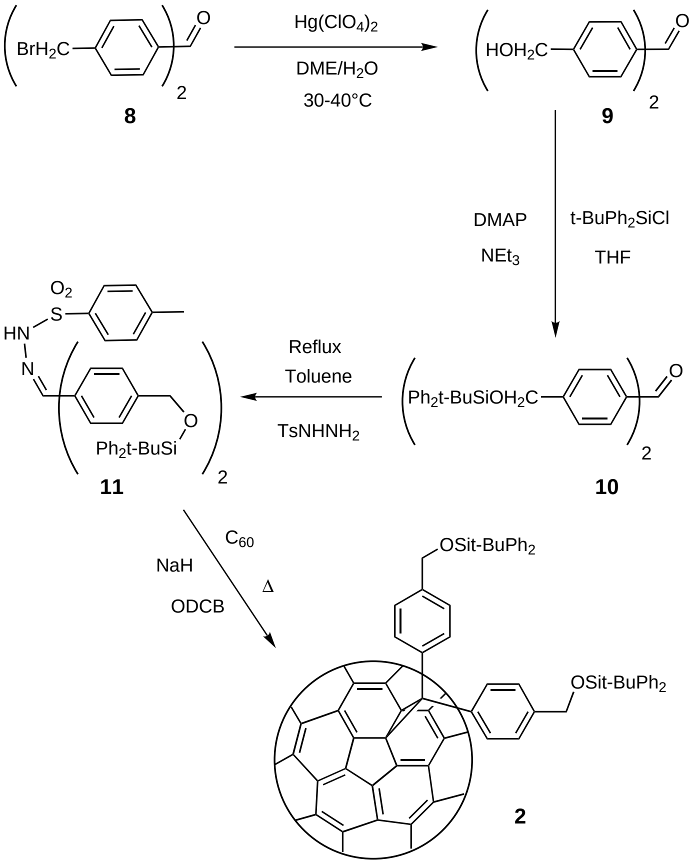
Methanofullerene syntheses: The methanofullerenes **1** and **2** have been prepared by the reaction of tosylhydrazone salts,[9] formed in situ, with C_{60}. The different steps in methanofullerene **1** synthesis are described in Scheme 1. Starting from *p*-dimethylbenzophenone, compound **4** was prepared with a 60% crude yield.[11] The white powder thus obtained is contaminated with terephthalic acid as by-product of the reaction (about 50%). Compound **4** was converted into **5** by phosphorus pentachloride, and pure **5** was obtained by fractional crystallization (corrected yield 72%).[12] Compound **5** was esterified by *tert*-butanol in the presence of pyridine, giving **6** (77.8% yield), which was converted to **7** by



Scheme 1. The synthesis of methanofullerene **1**.

tosylhydrazide in boiling ethanol (83 % yield). Molecule **7** reacts with C_{60}, in 1,2-dichlorobenzene (ODCB) and in the presence of NaH, to give methanofullerene **1** (47.6 % yield, single isomer after equilibration and satisfactory structure determination).[13]

The steps of the synthesis of methanofullerene **2** are depicted in Scheme 2. Compound **8**, prepared from *p*-dimethylbenzophenone,[14] was hydrolyzed to **9** with the assistance of mercuric ions[15] in dimethoxyethane/water (72 % yield). Derivative **9** was protected by *tert*-butyldiphenylsilylchloride[16] (71 % yield), then converted to **11** (87 % yield) with tosylhydrazide in boiling toluene. Tosyl hydrazone **11** reacts with C_{60}, in 1,2-dichlorobenzene and in the presence of NaH, to give methanofullerene **2** in 64 % yield (corrected; 25 % of starting C_{60} recovered), as a single isomer.



Scheme 2. The synthesis of methanofullerene **2**.

Methanofullerene **3** was synthesized according to Isaacs and Diederich[8] and converted into the most stable isomer,[3,4] the [6,6]-closed form, by heating. The characterization results were consistent with those previously obtained by these authors.

The purity of the [6,6]-ring bridged methanofullerenes **1**, **2**, and **3** was verified by chromatography, mass, infrared, ^1H and ^{13}C NMR spectroscopies. Complete details of the syntheses and characterization of the [6,6]-ring bridged methanofullerenes **1**, **2**, and **3** and of intermediate compounds are described in the Experimental Section.

Absorption spectra of the ground singlet state of the C_{61} derivatives

General characteristics: Room-temperature absorption spectra of the three methanofullerenes **1**, **2** and **3** in toluene and cyclohexane are shown in Figures 1a and 1b, respectively. In the visible region, the absorption spectra of the C_{61} methanofullerenes exhibit three distinct features whose principal peaks and molar absorption coefficients in toluene (Figure 1a) are:

for **1**: a sharp band at 432 nm (2410 $M^{-1}cm^{-1}$), a broad band peaking at 492 nm (1520 $M^{-1}cm^{-1}$), and a group of weak structures in the 650–700 nm region whose strongest feature is at 694 nm (219 $M^{-1}cm^{-1}$);

for **2**: similar features at 433 nm (2660 $M^{-1}cm^{-1}$), 490 nm (1910 $M^{-1}cm^{-1}$) and 698 nm (215 $M^{-1}cm^{-1}$);

for **3**: similar features at 429 nm (2620 $M^{-1}cm^{-1}$), 492 nm (1510 $M^{-1}cm^{-1}$) and 691 nm (195 $M^{-1}cm^{-1}$).

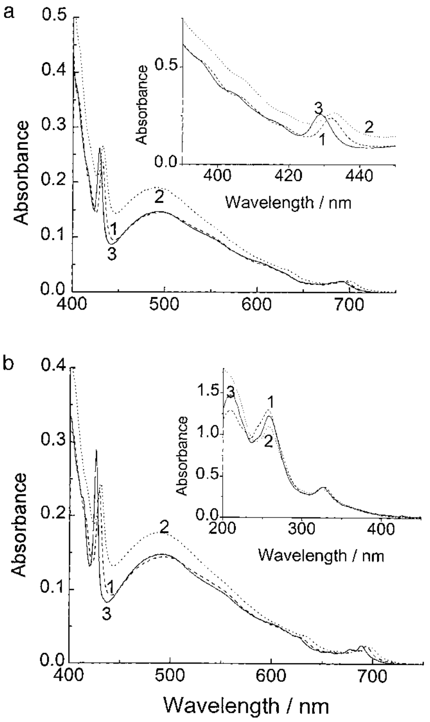


Figure 1. Ground-state absorption spectra, recorded at room temperature, of methanofullerenes **1**, **2**, and **3**: a) in toluene, 10^{-4} M, 400–750 nm (inset: detail of 380–450 nm region); b) in cyclohexane, 10^{-4} M, 400–750 nm (inset: 10^{-5} M, detail of 200–450 nm region).

In the aliphatic solvent cyclohexane, the corresponding band features are blue-shifted by 2–3 nm, and their absorption coefficients are slightly modified. The values for **3**, for example, are 426 nm (2900 $M^{-1}cm^{-1}$), 491 nm (1530 $M^{-1}cm^{-1}$) and 689 nm (252 $M^{-1}cm^{-1}$).

These three new bands, not present in C_{60}, are very similar to those reported for several other methanofullerenes.[7,8] The sharp band at ≈430 nm has been considered as characteristic of [6,6]-closed ring bridged methanofullerenes,[7] and is also present in dihydrofullerene[17] and cyclohexyl-fused pseudo-dihydrofullerenes.[17–19] This 430 nm peak is absent in [6,5] fulleroid structures.[7,20,21] The broad band peaking at around 500 nm is observed in [6,6]-closed ring fullerene structures where the adduct is linked to the fullerene by a Δ bridge (e.g., $C_{60}O$[22] and the closed-ring isomer of $C_{61}H_2$[23]) and is not exhibited in cyclohexyl-fused pseudo-dihydrofullerenes.[17–19] The longest wavelength absorption, around 700 nm for all methanofullerenes, is also present in cyclohexyl-fused pseudo-dihydrofullerenes.[17–19] Complex functional group effects on the spectra have been reported by Cardullo et al.[24] for multigrafted C_{60} with cyclopropyl- and cyclohexyl-fused functionalization.

It is striking that the sharp bands in the 400–410 nm region, which are characteristic structural features of C_{60}, are broadened and attenuated to become mere shoulders in the spectra of **1**, **2,** and **3** (Figure 1a, insert). Furthermore, in the latter the two sets of broad bands with maxima at ≈550 and ≈600 nm that are prominent in C_{60} spectra do not appear. Thus, these methanofullerene spectra are distinctively different from those of [6,5] ring-open methanofulleroids[3,20] for which spectral features similar to those of C_{60} are clearly observed in the visible spectral region.

On the other hand, the UV spectra of **1**, **2,** and **3** in cyclohexane (Figure 1b, insert) exhibit strong bands which are very similar to the strong features observed for C_{60} in this spectral region in *n*-hexane and at the same wavelengths and with similar absorption coefficients in cyclohexane.[25] The values for the three C_{61} derivatives are given in Table 1, where they are compared with the corresponding bands of C_{60}. Each of these compounds also has a strong band in the 210 nm region. Its absorption coefficient cannot be measured as accurately as for the other bands because of increased solvent absorption close to 200 nm. Note that the UV peak absorption coefficients of **1**, **2**, and **3** in cyclohexane are smaller than those of C_{60} in *n*-hexane or cyclohexane. The diminished value is consistent with loss of two π-type electrons in going from C_{60} (60 π-type electrons) to the [6,6] closed-ring methanofullerenes (58 π-type electrons).

Table 1. Ground-state absorption of C_{60} and the methanofullerenes **1**, **2**, and **3** in cyclohexane: peak wavelengths λ (nm) and absorption coefficients ε ($\mathrm{M}^{-1}\mathrm{cm}^{-1}$).

C_{60}		**1**		**2**		**3**	
λ	ε	λ	ε	λ	ε	λ	ε
257	158000	256	130000	258	110000	258	122000
329	49500	327	38000	326	33600	326	37000

These results suggest that the adduct strongly perturbs the numerous forbidden transitions of C_{60} that occur in the visible, and possibly gives rise to some new states (see later), whereas the allowed transitions in the ultraviolet are relatively less affected, in energy and in transition strength, by interaction of the adduct with the quasi-π system of electrons of the fullerene cage.

Towards specific assignments: After these general considerations, we now examine in more detail the perturbations induced by the adducts, in order to interpret the features observed in the visible-region spectra.

In C_{60}, the allowed $T_{1u}-{}^1A_g$ transitions, which occur in the UV below 400 nm, arise by excitation from the HOMO (symmetry h_u) to the second excited configuration, LUMO+1 (t_{1g}), as well as from HOMO − 1 (h_g) to LUMO (t_{1u}) excitations.[26] The visible-region forbidden transitions, induced by Herzberg–Teller vibronic interactions, occur by the lower-energy excitation from HOMO (h_u) to LUMO.[26]

Let us consider how the orbitals, electronic states, and transitions of C_{60} are transformed in going to methanofullerenes and methanofulleroids. In C_{60}, the t_{1g} LUMO is triply degenerate. Arias et al.[21] have deduced from electrochemical studies that this triple degeneracy appears to be approximately valid in methanofulleroid LUMOs, whereas in 58 π-electron methanofullerenes, the LUMO is approximately doubly degenerate. Indeed, methanofulleroids, which retain 60 π-type electrons, are considered to be isoelectronic with C_{60}.[10]

Further relevant information is provided by density-functional calculations carried out by Curioni et al.[27] on the structure and electronic properties of the two isomers (methanofullerene and fulleroid) of $C_{61}H_2$ using the local-density approximation. Their results show that although symmetry is lowered in $C_{61}H_2$ relative to (I_h) C_{60}, transitions to the LUMO-derived states remain dipole-forbidden because the character of the corresponding orbitals is hardly changed. This is consistent with the general weakness of the transitions observed in the visible region of methanofullerenes in our work. A particularly interesting result of the density functional calculations is that, in $C_{61}H_2$, the admixture of new states localized on the methylene group occurs at energies above that of states issuing from the LUMO+1 configuration. In the methanofullerene isomer, but not in the methanofulleroid variant, a new state occurs which has a large amplitude on the methylene group. This state could be responsible for the sharp band observed at ≈430 nm in $C_{61}H_2$ and analogously in other methanofullerenes which contain a bridge apex carbon. This assignment requires confirmation, in particular by many-body calculations of the excited molecular states.

We further note that a band at about 430 nm is not limited to methano-bridged methanofullerene compounds, since a similar band is also observed in di- and tetrahydrofullerenes and in pseudo-dihydrofullerene derivatives resulting from cycloadditions.[17,18,28] If there is a common electronic structural origin to this band in the different derivatives, which is not certain, it would probably be related to the existence of less than 60 π-type electrons on the carbon cages in each of these cases. In this connection, we note that the 430 nm band is not seen in methanofulleroids, which retain the 60 π-type electrons in an expanded fullerene system where the adduct hardly modifies the conjugated system of the C_{60} moiety. Further theoretical work is required in order to clarify the 430 nm band assignment.

Having examined the possible origin of the sharp band at ≈430 nm, we now consider interpretation of the broad band at ≈495 nm. As discussed above, the adducts to C_{60} mainly perturb the orbitals giving rise to Herzberg–Teller-induced forbidden transitions in the visible. Calculations show that the HOMO–LUMO gap in the prototype methanofullerene

$C_{61}H_2$ is not modified by more than 0.2 eV with respect to C_{60}.[27] We therefore suggest that the 495 nm band in the methanofullerenes is derived from one or more of the transitions corresponding to the γ and δ bands in the 500–620 nm region for C_{60}, that is, the $1^1T_{1g}-1^1A_g$, $1^1T_{2g}-1^1A_g$, $1^1T_{2u}-1^1A_g$[26] and possibly the $1^1G_g-1^1A_g$[29–31] transitions of the I_h molecule.

The group of weak features close to 700 nm could also be derived from one of these orbitally forbidden transitions in C_{60}. An alternative possibility is that the 700 nm features arise from a spin- (and possibly orbitally) forbidden transition to the lowest triplet state. A similar assignment has been proposed for the very much weaker bands of C_{60} in this region,[26] as well as, on the basis of theoretical calculations, for the similar but stronger bands observed in C_{60}–anthracene Diels–Alder adducts of C_{60}[32] and in $C_{60}H_2$.[17] It is our intention to eventually test this possible assignment experimentally.

Finally, it is of interest that oxo- and methylene-bridged C_{60} *dimers* have an essentially featureless absorption spectrum in the 400–700 nm visible region.[33] In these dimers, carbon–carbon bonds link two C_{60} molecules, and the oxygen atom or the carbon of the methylene group forms the apex of a bridge between these two cages. Although it is clear that this structure severely perturbs the LUMO and the states issuing from it, the dimer absorption spectra in the 200–400 nm region[33] show that perturbation of the configurations giving rise to the allowed transitions mainly affects their relative dipole oscillator strengths, but hardly effects their energies at all.

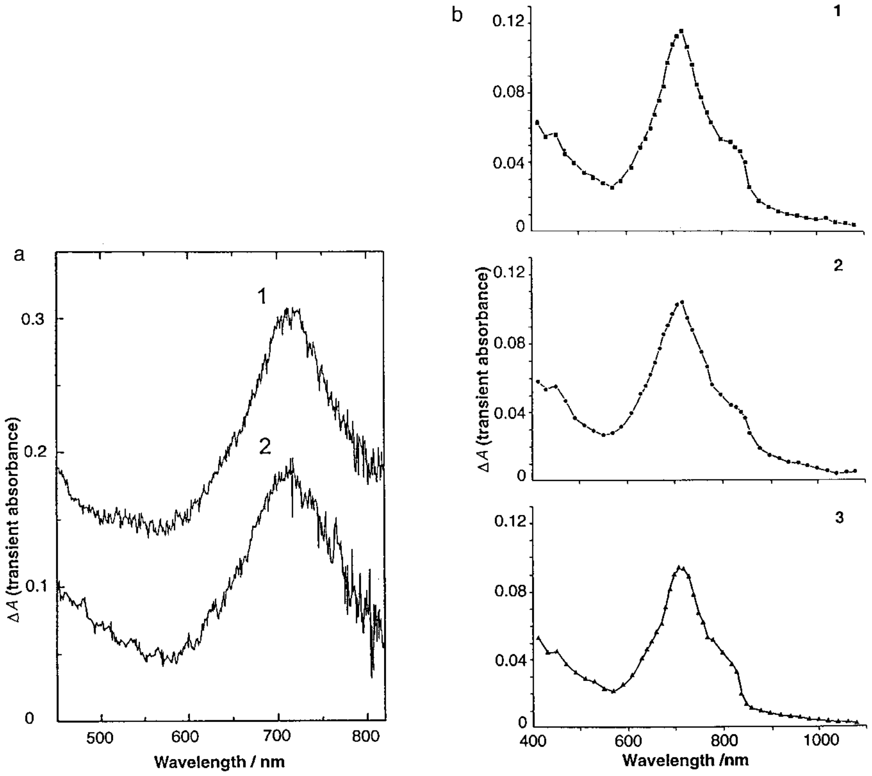


Figure 2. Triplet-minus-singlet difference absorption spectra of: a) **1** and **2** in toluene obtained by laser flash photolysis; and b) **1**, **2**, and **3** in benzene obtained by pulse radiolysis.

Triplet absorption spectra: Figure 2a shows the triplet-minus-singlet difference absorption spectra of **1** and **2** obtained by laser flash photolysis of simple $\approx 10^{-4}$ M solutions of the methanofullerenes in toluene; Figure 2b shows the same spectra, including that of **3**, obtained after pulse radiolysis of $\approx 10^{-4}$ M solutions of the methanofullerenes in benzene in the added presence of 10^{-1} M biphenyl as triplet sensitizer.

It can be seen that the absorption profiles of all three methanofullerenes are identical within experimental error, with a maximum located at $\approx$720 nm. The shape of this 720 nm absorption band is similar to that of the 750 nm absorption of C_{60}, except that for the methanofullerenes there is an additional shoulder around 820 nm. This blue shift by 30 nm of the triplet absorption maximum as compared to the 750 nm λ_{max} of C_{60} triplet absorption is also observed for other methanofullerenes, including $C_{61}(COOEt)_2$.[34] The blue shift is slightly larger for double and triple cyclopropanation of C_{60}, giving λ_{max} at 690 nm and 650 nm, respectively.[34,35] For a number of pseudo-dihydrofullerenes, including cyclohexyl-fused and fulleroproline derivatives, the triplet absorption maximum is located at $\approx$700 nm.[17,18,36–39]

The energies of the observed triplet–triplet absorption bands of C_{60} in the 300–800 nm region fit reasonably well with calculated values of allowed $^3H_u \leftarrow 1^3T_{2g}$ and $^3G_u \leftarrow 1^3T_{2g}$ transitions.[40] In particular, the strong 750 nm band can be assigned to the $2^3G_u \leftarrow 1^3T_{2g}$ transition. It appears likely that the 720 and 820 nm triplet–triplet absorption features of the three methanofullerenes are related to the $2^3G_u \leftarrow 1^3T_{2g}$ and $2^3H_u \leftarrow 1^3T_{2g}$ transitions of C_{60}, which are predicted to give rise to bands at 740 and 820 nm,[40] respectively, in this parent fullerene.

Determination of the quantum yield of singlet oxygen production: Methanofullerene-sensitized production of singlet oxygen, assessed by the amplitude of $^1O_2(^1\Delta_g)$ phosphorescence at 1270 nm, was compared with that obtained for C_{60}. The data for **1** given in Figure 3 allowed us to determine the ratio of the slope α_Δ^1 of $^1O_2$ production sensitized by **1** as a function of pulse energy, to that determined for $^1O_2$ production sensitized by C_{60}, chosen as standard, α_Δ^{st}. The quantum yield $\Phi_\Delta^1$of singlet oxygen production by the methanofullerene was then calculated from the slope ratio after correction for the corresponding absorbances A_{532} of the solutions at 532 nm, the laser excitation wavelength [Eq. (1)].

$$\Phi_\Delta^1 = (\alpha_\Delta^1/\alpha_\Delta^{st}) \times (A_{532}^{st}/A_{532}^1) \times \Phi_\Delta^{st} \quad (1)$$

The quantum yield of singlet oxygen production for C_{60}, Φ_Δ^{st}, being near unity,[41,42] Equation (1) enabled us to determine a Φ_Δ value for the three C_{61} fullerene derivatives of near unity (see Table 2), with a maximum error of 20%. Moreover, as Φ_Δ

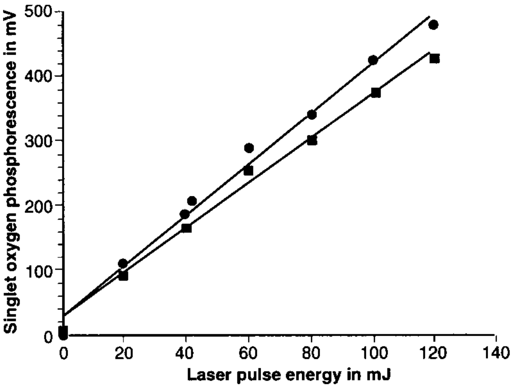


Figure 3. Photosensitized singlet oxygen production in oxygen-saturated perdeuterated toluene measured at its maximum concentration after the laser pulse and sensitized by the triplet of a) **1** (■), b) C_{60} (●) plotted as a function of laser pulse energy. ($A_{532} = 0.20$ and 0.24 for **1** and C_{60}, respectively, in a 1-cm cell).

Table 2. Quantum yield of methanofullerene-photosensitized production of $^1O_2(\Phi_\Delta)$ and molar absorption coefficients (ε_T in $\text{M}^{-1}\text{cm}^{-1}$) at the methanofullerene triplet maxima.

Methanofullerene	Φ_Δ	ε_T at 720 nm	
		laser flash photolysis	pulse radiolysis
1	1.04	14600	14000
2	0.96	13800	12000
3	0.95	–	15100

can only be smaller or equal to the quantum yield of triplet formation Φ_T, the Φ_T of the three C_{61} derivatives must also be near unity.

These high Φ_T and Φ_Δ values are similar to those observed for bis(carboethoxy)[61]fullerene, 1,2-epoxy[60]fullerene,[43] and cyclohexyl-fused [60]fullerenes.[17,36] It should be emphasized that functionalized fullerenes containing an electron-donating moiety can undergo a photoinduced intramolecular electron transfer process in polar solvents and exhibit a large decrease of singlet→triplet intersystem crossing.[38,39]

Determination of the triplet molar absorption coefficient

By laser flash photolysis: Using the comparative method,[44–46] it is possible to estimate the molar extinction coefficients of the C_{61} fullerene derivative triplets. The concentration of triplet molecules formed in the methanofullerene solution, with unknown triplet molar absorbance coefficient ε_T but known Φ_T (≈ 1), is compared with the concentration of triplet formed in a solution of C_{60} chosen as standard with known ε_T^{st} ($20200\,\text{M}^{-1}\text{cm}^{-1}$) at its 750 nm peak[40] and known Φ_T^{st} of near unity.[41,42] The maximum transient absorbance ΔA_T^{1} of the triplet of unknown molar absorption coefficient, and of the standard, ΔA_T^{st}, are plotted as a function of laser pulse energy (see Figure 4 for **1**). The slopes of these plots, α_T^{1} and α_T^{st}, are satisfactory straight lines. Furthermore, in the range of laser pulse energies used, the depletion of the ground state spans 1% to 10%; thus, we have favorable conditions for using the comparative method.[44–46] For solutions such that the ground state absorbance at 532 nm is A^1 for the unknown, and A^{st} for the standard, it can be easily shown[44–46] that Equation (2) holds, where ε_G is the molar

$$(\varepsilon_T - \varepsilon_G)\mathbf{1} = (\Phi_T^{st}/\Phi_T^{1}) \times (\alpha_T^{1}/\alpha_T^{st}) \times \varepsilon_T^{st} \times (A^{st}/A^{1}) \qquad (2)$$

absorption coefficient of the molecule in its ground state. From Equation (2) and the data shown in Figure 4, a triplet molar absorption coefficient of $14600 \pm 3000\,\text{M}^{-1}\text{cm}^{-1}$ at 720 nm was obtained for methanofullerene **1**, the ground-state absorption at this wavelength being negligible (see Figure 1). In an analogous manner, an ε_T of $13000 \pm 2600\,\text{M}^{-1}\text{cm}^{-1}$ at 720 nm was obtained for **2.**

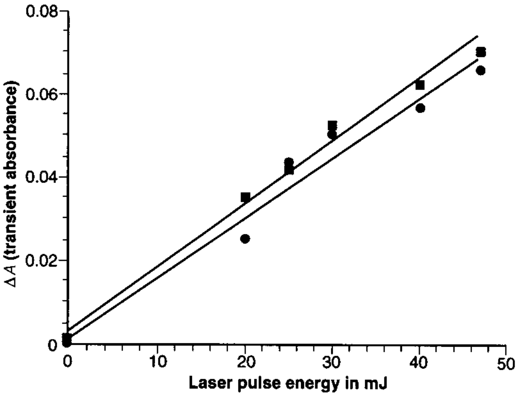


Figure 4. Maximum transient absorbances, ΔA_T^{1}, (■), 720 nm and ΔA_T^{st}, (●), 750 nm, plotted as a function of laser pulse energy. ($A_{532} = 0.17$ and 0.11 for **1** and C_{60}, respectively, in a 1-cm cell).

By pulse radiolysis: Independent estimates of the molar absorption coefficients of **1**, **2**, and **3** were obtained using the energy transfer method[46,47] and pulse radiolytic excitation. The lowest triplet of each methanofullerene in benzene was produced by energy transfer from the triplet excited state of another solute, biphenyl, with a well-characterized ε_T of $27100\,\text{M}^{-1}\text{cm}^{-1}$ at 365 nm,[47] present in greater concentration ($10^{-1}\,\text{M}$ versus $(1-2) \times 10^{-4}\,\text{M}$). Three reactions must be taken into account in this system:

1) Decay of the donor triplet ^3B to its ground state B_G: $^3B \xrightarrow{k_1} B_G$;
2) the energy-transfer reaction $^3B + C_{61} \xrightarrow{k_q} B_G + {}^3C_{61}$;
3) decay of the acceptor triplet $^3C_{61}$ to its ground state while it is being formed: $^3C_{61} \xrightarrow{k_3} C_{61}$.

Typical values of the rate constants obtained for methanofullerene **1** were $k_1 = 4.3 \times 10^4\,\text{s}^{-1}$, $k_2 = k_1 + k_q[C_{61}] = 1.12 \times 10^6\,\text{s}^{-1}$, and $k_3 = 3.34 \times 10^4\,\text{s}^{-1}$.

The maximum absorbance of $^3C_{61}$ at 720 nm reached at the end of the energy-transfer reaction, corrected for decay of the donor triplet ^3B by routes other than energy transfer, is given by Equation (3), and the maximum absorbance of $^3C_{61}$ corrected for decay of $^3C_{61}$ during its formation is given by Equation (4). The correction for decay of the ^{3}B state by

$$A_{720,cor} = A_{720,obs} \times [k_2/(k_2 - k_1)] \qquad (3)$$

$$A_{720,cor} = A_{720,obs} \times \exp[(\ln k_2/k_3)/(k_2/k_3 - 1)] \qquad (4)$$

routes other than energy transfer was typically ≈4%, and that for decay of $^3C_{61}$ during its formation was typically

≈11 %. The resulting estimate for methanofullerene **1** is given in Equation (5). This value is in good agreement with

$$\varepsilon_T(^3C_{61}) \text{ at } 720\text{ nm} = \varepsilon_T(^3B) \text{ at } 365\text{ nm} \times A_{720}(^3C_{61})/A_{365}(^3B) = 14\,000 \pm 1\,400\,\text{M}^{-1}\text{cm}^{-1} \qquad (5)$$

the corresponding molar absorption coefficient obtained in the above laser flash photolysis determination. The corresponding ε_T values obtained by pulse radiolysis for **2** and **3** are collected in Table 2.

This decrease of the triplet molar absorption coefficient compared with that of C_{60} has been observed for a number of C_{60} derivatives such as hydrofullerenes[17] and cyclohexyl-fused pseudo-dihydrofullerenes.[17,36,39]

Conclusion

Functionalization of C_{60} by different methanofullerene syntheses leads to molecules which might have very different chemical, mechanical, or solvatochromic properties.[3] However, as the electrochemical studies of Boudon et al. showed,[48] the sp^3 C atoms in the methano bridges of methanofullerenes can act as insulators and greatly reduce the effects of the nature of substituents. Our results on three very different functionalizations enable us to confirm that the photophysical properties of methanofullerenes could be rather similar in certain cases, at least when the functionalization does not involve an electron donor.[37,19] The sharp band at ≈430 nm in the $S_n \leftarrow S_0$ absorption spectrum could be linked to the existence of less than 60 π-type electrons on the carbon cages, since a similar band is observed in di- and tetrahydrofullerenes and in pseudo-dihydrofullerene derivatives resulting from cycloadditions,[17,18] but not in methanofulleroids; the latter retain the 60 π-type electrons in an expanded fullerene system. We further observe that the triplets of the three methanofullerenes we have studied have common general characteristics, namely: a) a triplet intersystem crossing efficiency Φ_T and a corresponding quantum yield of singlet oxygen production, Φ_Δ, near unity; b) a 30 nm hypsochromic shift of the main visible triplet absorption band as compared to the 750 nm main band of $^3C_{60}$ in toluene or benzene, lower than the 50 nm shift of a number of pseudo-dihydrofullerenes, including cyclohexyl-fused and fulleroproline derivatives;[17,18,36–39] and c) a lower (by ≈25 %) triplet molar absorption coefficient than that of $^3C_{60}$.

The fact that our methanofullerenes have similar quantum yields for singlet oxygen formation as does C_{60} itself suggests that such derivatization, avoiding a coupling with an electron donor, will not lower their biological photosensitization efficiency were they to be used, for example, in photodynamic therapy.[49] For such an application, appropriate adducts could be chromophores absorbing in the red spectral region of highest tissue transparency. Moreover, the possibility of varying the adduct provides the opportunity to modify the methanofullerene lipophilicity and consequently the site of intracellular delivery.

Experimental Section

Materials: Reagents used were the best available commercially. C_{60} was purchased from Technocarbo, Les Cyclades, Chemin de Camperousse, F-06130 Plan de Grasse (France). Tetrahydrofuran and toluene were distilled over sodium/benzophenone, 1,2-dichlorobenzene over calcium hydride, pyridine over potassium hydroxide, and *tert*-butanol over sodium. All other solvents were used as supplied (minimum purity 99 %).

Characterization: IR spectra were obtained on a Nicolet – Impact 400 D FTIR spectrometer. ^{1}H and ^{13}C NMR spectra were measured on a Bruker AC200 (250 MHz) instrument for the intermediate compounds and a Bruker Avance DRX400 (400 MHz) instrument for the methanofullerenes. Mass spectra were recorded on a Nermag R 10-10 S spectrometer [electron impact (EI) or chemical ionization by CH_4 or NH_3]. Chromatographic analysis was performed on a C18 Interchrom (150 × 4.6)-type ODS2 column and a Waters 600 E system controller equipped with a Waters 991 photodiode array detector (190 – 800 nm). Data were collected on a NEC Powermate SX/16 computer. Melting points were recorded on a Büchi 535 instrument. A Kontron model Uvikon 940 spectrophotometer was employed for spectral measurements of the ground-state C_{61} derivatives (bandwidth 0.3 nm, data interval 0.1 nm). The sources of solvents were: Prolabo RP, France (toluene); SDS, France (perdeuterated toluene); and Fluka, Switzerland (cyclohexane, solvent for luminescence spectroscopy).

Time-resolved spectroscopic methods: For the determination of the C_{61} fullerene triplet properties, we used the complementary time-resolved techniques of laser flash photolysis and pulse radiolysis. In the photolysis experiments we used frequency-doubled, 532 nm, 6 ns pulses emitted by a Nd:YAG laser (Quantel YG 585 10 G, France), at a frequency of 10 Hz. The detector for the triplet – triplet absorption was an OMA 3 built by Princeton Applied Research with detector interface model 1461, gated diode array model 1455 BHQ and pulse amplifier model 1304, interfaced with a Hewlett – Packard 9000 computer. The laser pulse energy was measured in mJ by a laser monitor (model 900) built by Laser Instrumentation. The detector for the $^1O_2$ phosphorescence emission with λ_{max} at 1.27 μm was a 3-mm diameter Judson J16 germanium photodiode, the resulting voltage being applied to a Judson amplifier and fed to a Nicolet model 206 digital oscilloscope. Each transient spectrum resulted from an accumulation of spectra produced by 100 laser shots. The solvent used for the $^1O_2$ measurements was [D$_8$]toluene, since the detection of $^1O_2$ in this solvent is facilitated by its relatively long intrinsic lifetime (≈ 320 μs). In the radiolysis measurements we used single 20 – 100 ns pulses of 9 – 12 MeV electrons delivered by a Vickers linear accelerator.[50,51] Analyzing light from a xenon lamp was passed through a Kratos monochromator onto an EMI 9558 Q photomultiplier for wavelengths between 350 and 780 nm, and a UDT PIN 10 photodiode between 780 and 1080 nm. Changes in absorbance with time were recorded with a Tektronix 7612 AD digitizer fitted with a DAN 486 DX 33 computer. Solutions of the methanofullerenes in benzene (Romil, super purity solvent) were contained in spectrosil quartz cells of 2.5 cm optical path length.

Bis(4-*tert*-butylbenzoate)methanone (6): Compound **5** (4.32 g, 14.1 mmol), anhydrous *tert*-butanol (6.6 mL), and anhydrous pyridine (5.4 mL) were refluxed under argon for 25 hours. After cooling, pyridinium hydrochloride was filtered off, and the filtrate was extracted with dichloromethane (100 mL) and washed with aqueous hydrochloric acid (0.1 M, 50 mL) and then water (50 mL). The organic extract was dried over sodium sulfate, and the solvents were evaporated off. Subsequent recrystallization from hexane afforded **6** as pure white crystals (4.175 g, 77.7 %, m.p. 122 °C). ^{1}H NMR (CDCl$_3$): $\delta = 7.91$ (d, 4H, $J = 8.25$ Hz), 7.62 (d, 4H, $J = 8.25$ Hz), 1.43 (s, 18H); ^{13}C NMR (CDCl$_3$): $\delta = 195.46$ (s), 164.71 (s), 140.15 (s), 135.46 (s), 129.64 (CH), 129.34 (CH), 81.76 (O – C), 28.07 (*t*Bu); IR (KBr): $\tilde{\nu} = 2999.1$, 2977.9, 2931.6, 2869.9, 1710.8, 1658.7, 1502.5, 1477.4, 1460.0, 1406.0, 1392.5, 1367.4, 1313.4, 1298.0, 1253.7, 1163.0, 1120.6, 1016.4, 929.6, 873.7, 848.6, 721.3 cm^{-1}; MS (NH$_3$): *m/z* (%) = 400 (100) $[M+NH_4]^+$, 383 (85) $[M+H]^+$, 327 $[M-t\text{Bu}+2]^+$, 309 (40); $R_f = 0.66$ (hexane/ethyl acetate:4/1).

Bis(4-*tert*-*b*utylbenzoate)methanotosylhydrazone (7): Diester **6** (2.31 g, 6.05 mmol, 1 equiv) in ethanol (80 mL) was refluxed under argon with tosylhydrazide (2.25 g, 12.1 mmol, 2 equiv) for 3 hours, then stirred at room temperature overnight. Ethanol was evaporated off, and crude **7** was purified by flash chromatography on silica gel with CH_2Cl_2 as eluant. After evaporation, pure **7** was obtained as white crystals (2.73 g, 82 %). ^{1}H NMR

($CDCl_3$): $\delta = 7.99$ peaks (2p, 2H), 7.72 (m, 4H), 7.48 (s, 1H), 7.31 (2p, 2H), 7.2 (2p, 2H), 7.05 (2p, 2H), 2.29 (s, 3H), 1.45 (2p, 18H); ^{13}C NMR ($CDCl_3$): $\delta = 165.06$, 164.51, 152.18, 144.39, 139.45, 135.21, 134.56, 133.79, 133.04, 130.86, 129.72, 129.3, 128.23, 127.87, 127.11, 81.85, 81.32, 28.09, 21.6; IR (KBr): $\tilde{\nu} = 3158.1$, 2977.7, 2931.4, 1710.7, 1596.9, 1477.3, 1458.0, 1405.9, 1368.3, 1351.0, 1311.4, 1298.9, 1256.5, 1185.1, 1168.7, 1121.5, 1054.9, 1018.3, 974.9, 882.3, 862.1, 846.6, 814.8, 782.0, 705.9, 681.8, 557.4, 549.6 cm^{-1}; MS (NH_3): m/z (%) = 551 (100) $[M+1]^+$; $R_f = 0.37$ (hexane/ethyl acetate: 4/1).

61,61-Bis[4-*tert*-butylbenzoate]-1,2-dihydro-1,2-methanofullerene[60] (1): C_{60} (0.885 g, 1.23 mmol, 1 equiv) was dissolved in anhydrous degassed 1,2-dichlorobenzene (250 mL), after which sodium hydride (60% in oil, 0.249 g) and **7** (0.686 g, 1.25 mmol, 1 equiv) were introduced. The mixture was heated stepwise (1 h at 50 °C, 2 h at 80 °C, 1 h at 100 °C, 1 h at 120 °C, 1 h at 140 °C, and 1 h at 160 °C) under argon. After cooling, the reaction mixture was quenched with water (150 mL), stirred for 5 min, and filtered on Celite®. The organic layer was decanted, washed with brine, and dried over sodium sulfate, and the solvents were evaporated off. Crude **1** was purified by flash chromatography on silica gel and eluted by hexane/toluene (4/6). After evaporation, pure **7** was obtained as a brown powder. The isomeric mixture was dissolved in chlorobenzene (100 mL) and refluxed for 2 days under argon. Chlorobenzene was evaporated, and **1** (single isomer) was obtained after chromatography as a brown powder (0.635 g, 47.6%). ^1H NMR ($CDCl_3$): $\delta = 8.17$ (d, 4H, $J = 8.5$ Hz), 8.10(d, 4H, $J = 8.5$ Hz), 1.59 (s, 18H); ^{13}C NMR ($CDCl_3$): $\delta = 165.10$, 147.42, 145.24, 145.21, 145.14, 144.73, 144.66, 144.54, 144.35, 143.81, 143.02, 142.96, 142.64, 142.14, 142.10, 140.98, 138.12, 132.02, 130.81, 130.06, 81.36, 78.22, 57.05, 28.19; IR (KBr): $\tilde{\nu} = 2971.4$, 1713.7, 1611.9, 1291.1, 1168.9, 1118.0, 720.8, 527.3 cm^{-1}; MS (NH_3): m/z (%) = 975 (1) $[M]^+$, 887 (10) $[M - 2(CO_2t\mathrm{Bu})]^+$, 720 (25) $[C_{60}]^+$, 224 (100); HPLC: $t_r = 3$ min (toluene/acetonitrile: 45/55), $t_r = 14.8$ min (toluene/acetonitrile: 35/65); UV/Vis (CH_2Cl_2): $\lambda_{max}(\varepsilon) = 223$ (128482), 259 (136168), $\lambda_{max}(\varepsilon) = 223$ (128000), 259 (136000), 329 nm (38000 $M^{-1}cm^{-1}$).

Bis[4-(hydroxymethyl)phenyl]methanone (9): Mercuric oxide[15] (6.55 g, 0.0302 mol, 2.09 equiv) was introduced into dimethoxyethane (79 mL), and then perchloric acid (70%) (5.6 mL, 9.352 g, 0.093 mol, 6.46 equiv) and water (2 mL) were added. The mixture was stirred for 20 min at a temperature between 40 and 60 °C. Distilled water (10 mL) and **8** (5.60 g, 0.0144 mol, 1 equiv) were then introduced. The mixture was stirred at 40–60 °C for 1 h. Water (100 mL), potassium chloride (10 g), and ethyl acetate (100 mL) were then introduced, and the mixture was stirred for a few minutes. Potassium perchlorate was filtered off and rinsed with ethyl acetate (20 mL). The mixture was then further extracted with ethyl acetate (2 × 100 mL). Organic extracts were pooled and washed with saturated aqueous potassium carbonate solution (50 mL), and the mercuric carbonate was filtered off. The organic layer was washed with brine (50 mL) and dried over sodium sulfate. The solution was then evaporated, and the resultant crude **9** was purified by flash chromatography on silica gel (hexane/ethyl acetate (1/1), then ethyl acetate). Solvents were evaporated, and pure **9** was obtained as a white solid (2.51 g, 72%). ^1H NMR ([D$_6$]DMSO): $\delta = 7.75$ (d, 2H, $J = 8.1$ Hz), 7.54 (d, 2H, $J = 8.1$ Hz), 4.76 (d, 2H, $J = 5.75$ Hz), 4.44 (t, 1H, $J = 7.75$ Hz), 2.84 (s, 3H); ^{13}C NMR ([D$_6$]DMSO): $\delta = 195.6$, 147.9, 136.0, 129.92, 126.94, 62.78; IR (KBr): $\tilde{\nu} = 3333.2$, 3244.5, 2912.7, 2858.7, 1647.3, 1608.7, 1412.0, 1311.7, 1288.5, 1145.5, 1114.9, 1087.9, 1045.5, 1014.6, 929.7, 856.4, 821.7, 748.4, 686.7, 628.8 cm^{-1}; MS (NH_3): m/z (%) = 260 (10) $[M+18]^+$, 243 (100) $[M+1]^+$, 135 (35).

Bis[4-(*tert*-butyldiphenylsilyloxymethyl)phenyl]methanone (10): Diol **9** (1.78 g, 7.36 mmol, 1 equiv) was dissolved in anhydrous tetrahydrofuran (25 mL), and then triethylamine (1.637 g, 16.18 mmol, 2.2 equiv) and 4-dimethylaminopyridine (0.090 g, 0.736 mmol, 0.1 equiv) were introduced. The mixture was stirred for a few seconds at 0° C. *tert*-Butyldiphenylsilylchloride[16] (4.448 g, 16.18 mmol, 2.2 equiv) was introduced, and the temperature was maintained at 0 °C for 2 h. The mixture was then stirred overnight at RT. Triethylammonium chloride was filtered off and washed with diethyl ether. Solvents were evaporated, and the resultant crude **10** was purified by flash chromatography on silica gel (hexane/ethyl acetate: 95/5, or pure toluene). Pure **10** was thus obtained as a colorless, very viscous oil (3.59 g, 71%). ^1H NMR ($CDCl_3$): $\delta = 7.68$ (m, 4H), 7.59 (m, 8H), 7.11 (m, 16H), 4.74 (s, 4H), 1.01 (s, 18H); ^{13}C NMR ($CDCl_3$): $\delta = 196.27$, 145.77, 136.42, 135.53, 133.20, 130.15, 129.80, 127.79, 125.54, 65.14, 26.81, 19.3; IR (NaCl) $\tilde{\nu} = 3070.5$, 3049.3, 2958.6, 2931.6, 2891.1, 2858.3, 1656.8, 1608.75, 1471.6, 1427.2, 1375.2, 1361.7, 1309.6, 1278.7, 1207.4, 1111.1, 929.7, 825.6, 744.6, 702.1, 609.5 cm^{-1}; MS (NH_3): m/z (%) = 736 (20) $[M+18]^+$, 720 (65) $[M+2]^+$, 719 (100) $[M+1]^+$, 274 (80); $R_f = 0.59$ (SiO_2/toluene).

Bis[4-(*tert*-butyldiphenylsilyloxymethyl)phenyl]methanotosylhydrazone (11): Compound **10** (2.824 g, 3.9 mmol, 1 equiv), *p*-toluenesulfonylhydrazide (0.904 g, 4.8 mmol, 1.2 equiv) and toluene (100 ml) were refluxed for 2 days under argon. Toluene was evaporated off under reduced pressure down to 5 mL, and crude **11** was purified by flash chromatography on silica gel (toluene) to yield pure **11** as a colorless, very viscous oil (2.2 g, 87%), which solidified on standing. ^1H NMR ($CDCl_3$): $\delta = 8.04$ (2p, 2H), 7.87 (m, 8H), 7.56 (m, 20H), 7.24 (2p, 2H), 5.01 (s, 2H), 4.92 (s, 2H), 1.31 (s, 9H), 1.25 (s, 9H); ^{13}C NMR ($CDCl_3$): $\delta = 154.35$, 144.07, 143.29, 143.04, 135.58, 135.51, 135.20, 133.32, 133.14, 129.87, 129.74, 129.66, 129.57, 128.19, 127.91, 127.82, 127.74, 127.57, 127.08, 125.64, 65.12, 64.97, 26.66, 26.80, 21.61, 19.30; IR (KBr): $\tilde{\nu} = 3436$, 3217, 3070, 2957, 2930, 2889, 2857, 1653, 1616, 1595, 1472, 1432, 1381, 1349, 1169, 1122, 1091, 825, 741, 715, 664, 610, 554, 512 cm^{-1}; MS (NH_3): m/z (%) = 887 (75) $[M+1]^+$, 274 (25), 206 (25), 204 (30), 190 (50), 189 (45), 174 (100), 156 (10); $R_f = 0.29$ (hexane/ethyl acetate 9:1) or 0.25 (toluene).

61,61-Bis[4-(*tert*-butyldiphenylsilyloxymethyl)phenyl]-1,2-dihydro-1,2-methanofullerene[60] (2): C_{60} (0.2 g, 0.277 mmol, 1 equiv) was dissolved under argon in anhydrous, degassed 1,2-dichlorobenzene (50 mL), after which **11** (0.26 g, 0.293 mmol, 1.3 equiv) and sodium hydride (60% in oil, 0.041 g, 1.03 mmol) were added. The mixture was heated stepwise (1.5 h at 50 °C, 2 h at 80 °C, 1 h at 100 °C, 1 h at 120 °C, 1 h at 140 °C and 1 h at 160 °C) under argon. After cooling, the reaction mixture was quenched with water (150 mL), stirred for 5 min and filtered on Celite®. The organic layer was decanted, washed with brine, and dried over sodium sulfate, and the solvents were evaporated off. Crude **2** was purified by flash chromatography on silica gel and eluted by hexane/toluene (4/1) to obtain pure **2** (single isomer shown by HPLC, confirmed by NMR) as a brown powder (0.395 g, 25% of starting C_{60} recovered, 64% yield). ^1H NMR ($CDCl_3$): $\delta = 8.125$ (2p, 4H), 7.75 (m, 8H), 7.45 (m, 16H), 4.89 (s, 4H), 1.18 (s, 18H); ^{13}C NMR ($CDCl_3$): $\delta = 148.42$, 145.41, 145.17, 145.08, 144.69, 144.64, 144.61, 144.24, 143.84, 143.00 (C_{60}), 142.91, 142.27, 142.11, 141.00, 140.84, 138.20, 137.64, 135.59, 133.29, 130.75, 129.75, 129.03, 128.22, 127.74, 126.16, 79.18, 65.18, 58.03, 26.91, 19.34; IR (KBr): $\tilde{\nu} = 3067$, 3046, 3024, 2955, 2928.34, 2886.15, 2854.58, 1510, 1462, 1426, 1373, 1208, 1184, 1110.1, 1085.6, 1018, 823, 739, 701.3, 606, 575, 555, 526, 505 cm^{-1}; MS (NH_3): m/z (%) = 1441 (75) $[M+NH_4]^+$, 1424 (20) $[M+1]^+$, 1383 (10) $[M - 40]^+$, 720 (30), 272 (50), 216 (100); HPLC: $t_r = 7.17$ min (toluene/acetonitrile: 45/55).

61-[(Ethoxycarbonyl)methylcarboxylate]-1,2-dihydro-1,2-methanofullerene [60] (3): This compound was synthesized according to the method of Isaacs and Diederich.[8] The characterization results were consistent with those previously obtained by these authors.

Acknowledgments: A.R. and S.R. acknowledge the financial aid of Igol Île de France. We also appreciate support from the European Community HCM program contracts CHRXCT 930178 (R.V.B.) and 94-0614 (R.V.B., S.L.), CNRS program GDR C_{60}, (A.R., S.L., R.V.B.) and of the Cancer Research Campaign (E.J.L.). We are grateful to D. Allan and B. W. Hodgson for the maintenance of the pulse radiolysis equipment at the Paterson Institute for Cancer Research Free Radical Research Facility, Manchester (UK), operated with the support of the European Commission through the Access to Large-Scale Facilities activity of the TMR Program.

Received: June 13, 1997 [F726]

---

[1] T. Suzuki, Q. Li, C. Khemani, F. Wudl, Ö. Almarson, *Science* **1991**, *254*, 1186–1188.

[2] F. Diederich, Y. Rubin, *Angew. Chem.* **1992**, *104*, 1123–1146; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1101–1123.

[3] F. Diederich, L. Isaacs, D. Philp, *Chem. Soc. Rev.* **1994**, 243–255.

[4] F. Diederich, C. Thilgen, *Science* **1996**, *271*, 317–323.

[5] F. Djojo, A. Herzog, I. Lamparth, F. Hampel, A. Hirsch, *Chem. Eur. J.* **1996**, *2*, 1537–1547.

[6] A. S. Boutorine, H. Tokuyama, M. Takasugi, H. Isobe, E. Nakamura, C. Hélène, *Angew. Chem.* **1994**, *106*, 2526–2529; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2462–2465.

[7] L. Isaacs, A. Wehrsig, F. Diederich, *Helv. Chim. Acta* **1993**, *76*, 1231–1250.

[8] L. Isaacs, F. Diederich, *Helv. Chim. Acta* **1993**, *76*, 2454–2464.

[9] J. C. Hummelen, B. W. Knight, F. Lepeq, F. Wudl, *J. Org. Chem.* **1995**, *60*, 532–538.

[10] M. Prato, V. Lucchini, M. Maggini, E. Stimplf, G. Scorrano, M. Eiermann, T. Suzuchi, F. Wudl, *J. Am. Chem. Soc.* **1993**, *115*, 8479–8480.

[11] N. K. Moshchinskaya, N. F. Silin, E. E. Dmitrenko, V. A. Liberzon, G. B. Lokshin, A. M. Korchagina, *Neftekhina* **1962**, *2*, 541–549; *Chem. Abstr.* **1963**, *59*, 1521a.

[12] I. K. Kozinenko, A. F. Lebedev, *Vestn. Kiev. Politekh. Inst. Ser. Khim. Technol.* **1966**, *2*, 54–57; *Chem. Abstr.* **1968**, *68*, 30210q.

[13] H. Tomioka, K. Yamamoto, *J. Chem. Soc. Perkin Trans. 1* **1996**, 63–66.

[14] H.-F. Grützmacher, W. Husemann, *Tetrahedron* **1987**, *43*, 3205–3211.

[15] A. McKillop, M. E. Ford, *Tetrahedron* **1974**, *30*, 2467–2475.

[16] S. Hanessian, P. Lavallee, *Can. J. Chem.* **1975**, *53*, 2975–2977.

[17] R. V. Bensasson, E. Bienvenue, J.-M. Janot, S. Leach, P. Seta, D. I. Schuster, S. R. Wilson, H. Zhao, *Chem. Phys. Lett.* **1995**, *245*, 566–570.

[18] Y. Nakamura, T. Minowa, S. Tobita, H. Shizuka, J. Nishimura, *J. Chem. Soc. Perkin Trans. 2* **1995**, 2351–2357.

[19] Y. Z. An, J. L. Anderson, Y. Rubin, *J.Org. Chem.* **1993**, *58* , 4799–4801.

[20] M. Eiermann, F. Wudl, M. Prato, M. Maggini, *J. Am. Chem. Soc.* **1994**, *116*, 8364–8365.

[21] F. Arias, L. Echegoyen, S. R. Wilson, Q. Lu, Q. Lu, *J. Am. Chem. Soc.* **1995**, *117*, 1422–1427.

[22] K. M. Creegan, J. L. Robbins, W. K. Robbins, J. M. Millar, R. D. Sherwood, P. J. Tindall, D. M. Cox, A. B. Smith III, J. P. McCauley, Jr., D. R. Jones, R. T. Gallagher, *J. Am. Chem. Soc.* **1992**, *114*, 1103–1105.

[23] A. B. Smith, III, R. M. Strongin, L. Brard, G. T. Furst, W. J. Romanow, *J. Am. Chem. Soc.* **1993**, *115*, 5829–5830.

[24] F. Cardullo, P. Seiler, L. Issacs, J.-F. Nierengarten, R. F. Haldiman, F. Diederich, T. Mordsani-Denti, W. Thiel, C. Boudon, J.-P. Gisselbrecht, M. Gross, *Helv. Chim. Acta* **1997**, *80*, 343–371.

[25] R. V. Bensasson, E. Bienvenüe, M. Dellinger, S. Leach, P. Seta, *J. Phys. Chem.* **1994**, *98*, 3492–3500.

[26] S. Leach, M. Vervloet, A. Desprès, E. Bréheret, J. P. Hare, T. J. Dennis, H. W. Kroto, R. Taylor, D. R. M. Walton, *Chem. Phys.* **1992**, *160*, 451–466.

[27] A. Curioni, P. Giannozzi, J. Hutter, W. Andreoni, *J. Phys. Chem.* **1995**, *99*, 4008–4014.

[28] C. C. Henderson, P. A. Cohill, *Science* **1993**, 259, 1885–1887.

[29] D. J. van den Heuvel, G. J. B. van den Berg, E. J. J. Groenen, J. Schmidt, I. Holleman, G. Meijer, *J. Phys. Chem.* **1995**, *99*, 11644–11649 .

[30] F. Negri, G. Orlandi, F. Zerbetto, *J. Phys. Chem.* **1996**, *100*, 10849–10853.

[31] A. Sassara, G. Zerza, M. Chergui, *J. Phys. B.: At. Mol. Opt. Phys.* **1996**, *29*, 4997–5013.

[32] L. Udvardi, P. R. Surjan, J. Kürti, S. Pekker, *Synth. Metals* **1995**, *70*, 1377–1378.

[33] A. B. Smith III, H. Tokuyama, R. M. Strongin, G. T. Furst, W. J. Romanow, *J. Am. Chem. Soc.* **1993**, *117* 9359–9360.

[34] D. M. Guldi, H. Hungerbühler, K.-D. Asmus, *J. Phys. Chem.* **1995**, *99*, 9380–9385.

[35] D. M. Guldi, K.-D. Asmus, *J. Phys. Chem.* **1997**, *101*, 1472–1481.

[36] J. L. Anderson, Y.-Z. An, Y. Rubin, C. S. Foote, *J. Am. Chem. Soc.* **1994**, *116*, 9763–9764.

[37] D. M. Guldi, M. Maggini, G. Scorrano, M. Prato, *J. Am. Chem. Soc.* **1997**, *119*, 974–980.

[38] R. M. Williams, J. M. Zwier, J. W. Verhoeven, *J. Am. Chem. Soc.* **1995**, *117*, 4093–4099.

[39] P. A. Liddell, J. P. Sumida, A. N. MacPherson, L. Noss, G. R. Seely, K. N. Clark, A. L. Moore, T. A. Moore, D. Gust, *Photochem. Photobiol.* **1994**, *60* , 537–541.

[40] R. V. Bensasson, T. Hill, C. Lambert, E. J. Land, S. Leach, T. G. Truscott, *Chem. Phys. Letters* **1993**, *201*, 326–335.

[41] J. W. Arbogast, A. P. Darmanyan, C. S. Foote, Y. Rubin, F. N. Diederich, M. M. Alvarez, S. J. Anz, R. L. Whetten, *J. Phys. Chem.* **1991**, *95*, 11–12.

[42] M. Terazima, N. Hirota, H. Shiginohara, Y. Saito, *J. Phys. Chem.* **1991**, *95*, 9080–9085.

[43] T. Hamano, K. Okuda, T. Maschino, M. Hirobe, K. Arakane, A. Ryu, S. Mashiko, T. Nagano, *Chem. Commun.* **1997**, 21–22.

[44] B. Amand, R. V. Bensasson, *Chem. Phys. Lett.* **1975**, *34*, 44–48.

[45] R. V. Bensasson, C. R. Goldschmidt, E. J. Land, T. G. Truscott, *Photochem. Photobiol.* **1978**, *28*, 277–281.

[46] R. V. Bensasson, E. J. Land, T. G. Truscott, *Excited States and Free Radicals in Biology and Medicine—Contributions from Flash Photolysis and Pulse Radiolysis*, Oxford University Press, Oxford, **1993**, pp. 76–79.

[47] R. Bensasson, E. J. Land, *Trans. Faraday Soc.* **1971**, *67*, 1904–1915.

[48] C. Boudon, J.-P. Gisselbrecht, M. Gross, L. Isaacs, H. L. Anderson, R. Faust, F. Diederich, *Helv. Chim. Acta* **1995**, *78*, 1334–1344.

[49] *Photodynamic Therapy of Neoplastic Disease* (Ed.: D. Kessel), CRC, Boston, **1990**.

[50] J. P. Keene, *J. Sci. Instr.* **1964**, *41*, 493–496.

[51] J. Butler, B. W. Hodgson, B. M. Hoey, E. J. Land, J. S. Lea, E. J. Lindley, F. A. P. Rushton, A. J. Swallow, *Radiat. Phys. Chem.* **1989**, *34*, 633–646.