Restricted Rotation in (Phenylpyrrolidino)fullerene Derivatives

Fettah Ajamaa,[a][‡] Teresa M. Figueira Duarte,[a][‡] Cyril Bourgogne,[b] Michel Holler,[a] Patrick W. Fowler,[c] and Jean-François Nierengarten*[a][‡]

Keywords: Conformational studies / Cycloaddition / Fullerene / Restricted rotation

A complete series of (phenylpyrrolidino)fullerene derivatives has been prepared. A detailed conformational analysis of these compounds has been carried out by variable-temperature ^{1}H NMR experiments and computational studies. In the case of (phenylpyrrolidino)fullerene derivatives without *ortho* substituents, dynamic phenomena arising from restricted rotation around the phenyl–pyrrolidine bond are observed. In contrast, as soon as one of the *ortho* positions of the phenyl ring is substituted, the rotational energy barrier is high enough to prevent observation under our experimental conditions (room temperature to 120 °C) of any dynamic exchange resulting from rotation of the phenyl substituent on the pyrrolidine ring. Whereas, in principle, two diastereoisomeric conformers can exist for the *ortho*-substituted (phenylpyrrolidino)fullerenes, only the atropisomers in which the unsubstituted *ortho* position is located atop the fullerene sphere are obtained. We conclude that the reaction of the *ortho*-substituted benzaldehyde derivatives with C_{60} is diastereoselective, affording only one of the two possible atropisomers.

Introduction

Following the discovery of the macroscopic-scale [60]fullerene synthesis by Krätschmer, Huffman and co-workers in 1990,[1] the chemistry of this fascinating spherical molecule has been intensively investigated.[2] It is now well established that the chemical reactivity of [60]fullerene is typical of an electron-deficient olefin.[2] Indeed [60]fullerene reacts readily with nucleophiles and is a reactive 2π component in cycloadditions. Of the large number of reactions used for the functionalization of C_{60}, the 1,3-dipolar cycloaddition of azomethine ylides has been found to be particularly useful for the preparation of fullerene derivatives owing to its versatility and the ready availability of the starting materials.[3] The reaction is fast and clean, and pyrrolidinofullerenes are usually obtained in fair-to-good yields. As part of our research program on the synthesis and the study of fullerene-based materials,[4] we have noticed that in phenyl-substituted pyrrolidinofullerene derivatives, the NMR signals arising from the protons of the phenyl group attached to the pyrrolidine ring are usually broadened at room temperature by restricted rotation.[5] Similar observations have been reported by other research groups.[6] However, a systematic conformational study on such fullerene derivatives has not been reported so far. In this paper, we now describe the synthesis of a complete series of phenyl-substituted pyrrolidinofullerenes and a detailed conformational analysis based on variable-temperature ^{1}H NMR experiments and computational studies.

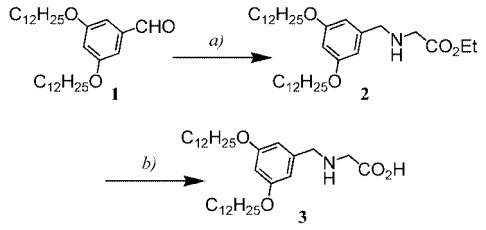
[a] Groupe de Chimie des Fullerènes et des Systèmes Conjugués, Ecole Européenne de Chimie, Polymères et Matériaux, Université Louis Pasteur et CNRS,
25 rue Becquerel, 67087 Strasbourg Cedex 2, France
E-mail: jfnierengarten@chimie.u-strasbg.fr
[b] Institut de Physique et Chimie des Matériaux de Strasbourg, Université Louis Pasteur et CNRS,
23 rue du Loess, 67037 Strasbourg, France
[c] Dept. of Chemistry, University of Exeter,
Stocker Road, EX4 4QD, U. K.
[‡] New address: Groupe de Chimie des Fullerènes et des Systèmes Conjugués, Laboratoire de Chimie de Coordination du CNRS,
205 route de Narbonne, 31077 Toulouse Cedex 4, France
E-mail: jfnierengarten@lcc-toulouse.fr

Results and Discussions

Synthesis

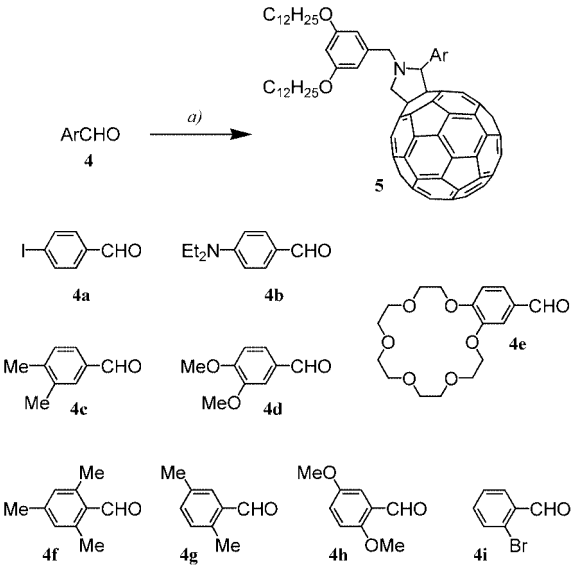
The most widely used approach for generating azomethine ylides preparatory to functionalization of [60]fullerene is the decarboxylation of imminium salts derived from the condensation of *N*-methylglycine (sarcosine) and an aldehyde. The scope of this reaction is very broad, and (*N*-methylpyrrolidino)fullerenes are efficiently produced by this route.[3] In the present study, we have decided to use *N*-(3,5-didodecyloxybenzyl)glycine rather than sarcosine. In fact, the 3,5-didodecyloxybenzyl group has proven to be a good solubilizing group for fullerene derivatives[7] and should prevent solubility problems for the targeted (phenylpyrrolidino)fullerenes. The preparation of the *N*-alkylated glycine derivative is depicted in Scheme 1. Reductive amination of 3,5-didodecyloxybenzaldehyde (**1**) with glycine ethyl ester hydrochloride furnished **2** in 79% yield. Subsequent treatment with KOH in THF/EtOH/H_2O gave *N*-(3,5-didodecyloxybenzyl)glycine (**3**) in quantitative yield.

  DOI: 10.1002/ejoc.200500315



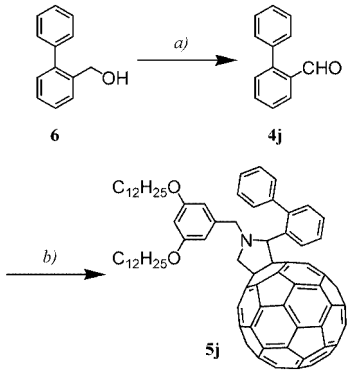
Scheme 1. Reagents and conditions: (a) glycine ethyl ester hydrochloride, Et_3N, EtOH, THF, molecular sieves (3 Å), room temp., then $NaBH_4$, 0 °C to room temp. (79%); (b) KOH, H_2O, EtOH, THF, room temp., then HCl (99%).

The preparation of the (phenylpyrrolidino)fullerene derivatives from C_{60}, **3** and various benzaldehydes is depicted in Scheme 2. Reaction conditions were adjusted for 3,4-dimethoxybenzaldehyde (**4d**). We first tried the classical conditions for the preparation of (*N*-methylpyrrolidino)fullerenes.[3] Treatment of **3** with aldehyde **4d** in the presence of C_{60} in refluxing toluene led to the formation of the desired fullerene derivative **5d** in 37% yield, albeit from a slow reaction (72 h). This result prompted us to change toluene for a solvent with a higher boiling point, namely *o*-dichlorobenzene (ODCB). Furthermore, the solubility of C_{60} is much higher in ODCB, allowing us to work at higher concentrations. When the reaction between **3**, **4d** and C_{60} was performed in refluxing ODCB, the reagents were completely consumed after 12 h and compound **5d** was thus obtained in 40% yield. These conditions were used for the preparation of all the substituted [*N*-(3,5-didodecyloxybenzyl)pyrrolidino]fullerene derivatives described in this paper. The starting benzaldehydes **4a**–**i** are commercially available, apart from **4e** which was prepared in two steps from pentaethyleneglycol according to a previously reported procedure.[8] The (phenylpyrrolidino)fullerene derivatives **5a**–**i** were obtained in yields of 34–54% by reaction of C_{60} with **4a**–**i** and **3** in refluxing ODCB.



Scheme 2. Reagents and conditions: (a) C_{60}, **3**, ODCB, 180 °C (34–54%).

Pyrrolidinofullerene **5j** was obtained in two steps from 2-phenylbenzyl alcohol (**6**) as depicted in Scheme 3. MnO_2 oxidation of **6** and subsequent reaction of the resulting benzaldehyde **4j** with **3** and C_{60} in refluxing ODCB yielded **5j**. In spite of the presence of a bulky substituent in the *ortho* position of the reactive aldehyde function in **4j**, pyrrolidinofullerene **5j** was obtained in a good yield (50%).



Scheme 3. Reagents and conditions: (a) MnO_2, CH_2Cl_2, room temp. (87%); (b) C_{60}, **3**, ODCB, 180 °C (50%).

Conformational Studies

The ^1H NMR spectra of the pyrrolidinofullerene derivatives **5a** and **5b** bearing *p*-substituted phenyl substituents are in full agreement with the C_1 symmetry resulting from the presence of a stereogenic center in the pyrrolidine ring. At room temperature the spectra exhibit the expected features with the characteristic signals arising from the dodecyl chains, an AB quadruplet for the benzylic CH_2 unit, an AB quadruplet and a singlet for the pyrrolidine protons. For both **5a** and **5b**, the signals corresponding to the protons of the phenyl group directly attached to the pyrrolidine ring are broad at room temperature. A variable-temperature NMR study showed clear coalescence, and the reversible narrowing of all these peaks reveals a dynamic effect. This indicates restricted rotation of the phenyl substituent on the pyrrolidine ring; the activation free energy of the rotation was estimated as $\Delta G^{\ddagger}$ = 13 kcal mol^{-1} by monitoring the coalescence of the aromatic C–H signals. As typical examples, the ^1H NMR spectra of compound **5a** recorded at different temperatures are shown in Figure 1. At high temperatures, an AA′XX′ system is seen for the aromatic protons of the *p*-iodophenyl unit. Indeed, the exchange between $H_{o/m}$ and $H_{o'/m'}$ is fast on the NMR timescale under these conditions, and both pairs of protons $H_o/H_{o'}$ and $H_m/H_{m'}$ appear equivalent in the ^1H NMR spectrum. In contrast, by cooling the solution to –50 °C, this exchange resulting from the rotation of the *p*-iodophenyl unit around the phenyl–pyrrolidine bond becomes slow on the NMR timescale, as attested by the four sets of signals observed for the aromatic protons H_o, $H_{o'}$, H_m and $H_{m'}$.

Computational studies were performed to evaluate the relationship between potential energy and the dihedral angle between the *p*-substituted phenyl ring and the pyrrolid-

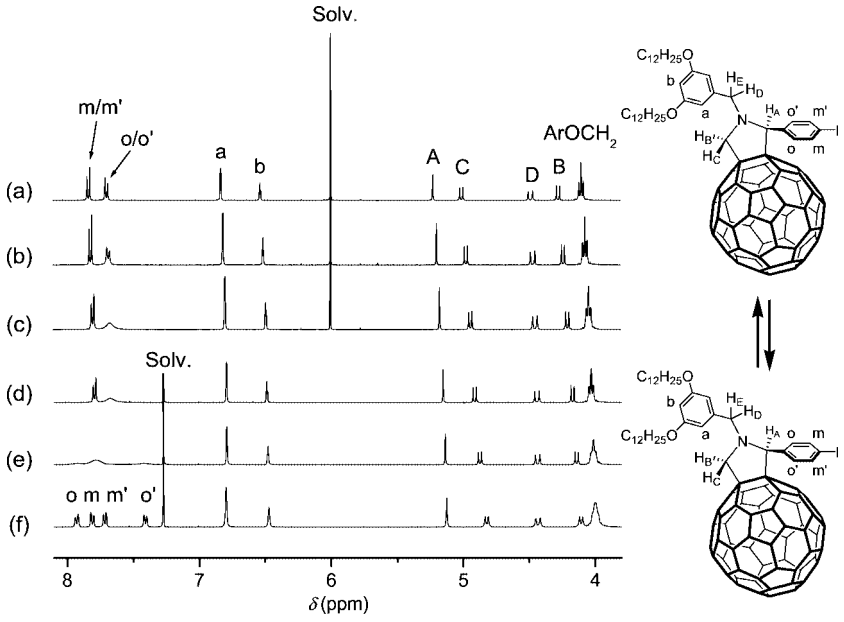


Figure 1. ^{1}H NMR spectra (400 MHz) of **5a** recorded in $CDCl_2CDCl_2$ at 100 °C (a), 50 °C (b) and 30 °C (c) and in $CDCl_3$ at 20 °C (d), –10 °C (e) and –50 °C (f).

inofullerene moiety (Figure 2). The molecular geometry was optimized at the AM1 semi-empirical level with fixed values of the torsion angle for rotation about the bond between the pyrrolidine ring and the attached aromatic group. This angle was increased stepwise from 0 to 360°, leading to the potential energy diagram shown in Figure 2 for compound **5b**. It is noteworthy that the calculated rotational energy barrier for rotation of the phenyl substituent on the pyrrolidine ring is ca. 15 kcal mol^{-1}, in good agreement with the value deduced from the NMR measurements.

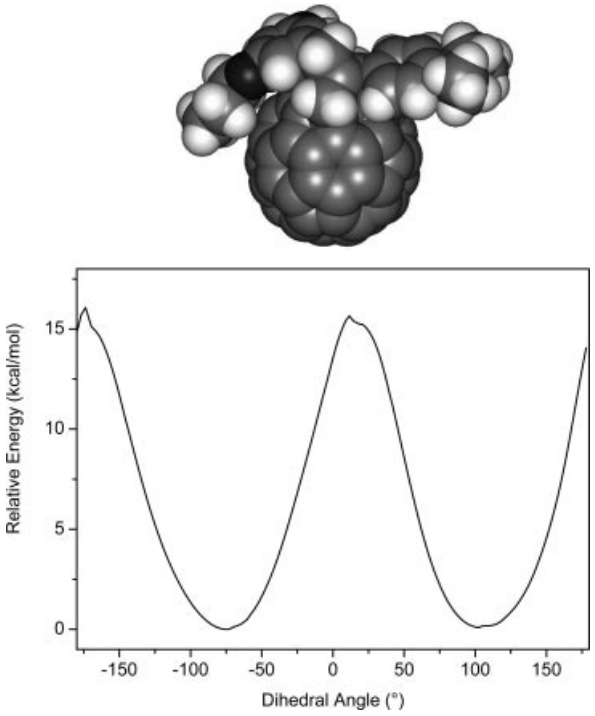


Figure 2. Bottom: calculated potential energy diagram of compound **5b** for rotation about the bond between the pyrrolidine ring and the phenyl group attached to it (the dodecyl chains have been replaced by propyl chains in the calculations). Top: theoretical structure of the most stable conformer.

The ^{1}H NMR spectrum of compound **5f** is well resolved at room temperature, with sharp signals for the protons of the mesityl unit (Figure 3). The two sets of aromatic signals and the three singlets observed for the mesityl group show that rotation around the mesityl–pyrrolidine bond is either slow on the NMR timescale or does not occur at all. Unambiguous assignment was achieved on the basis of 2D-COSY and NOESY spectra. It is worth noticing that the signal of the CH_3 group located atop the fullerene unit (Me_H) is observed at δ = 3.24 ppm and is shifted dramatically down-

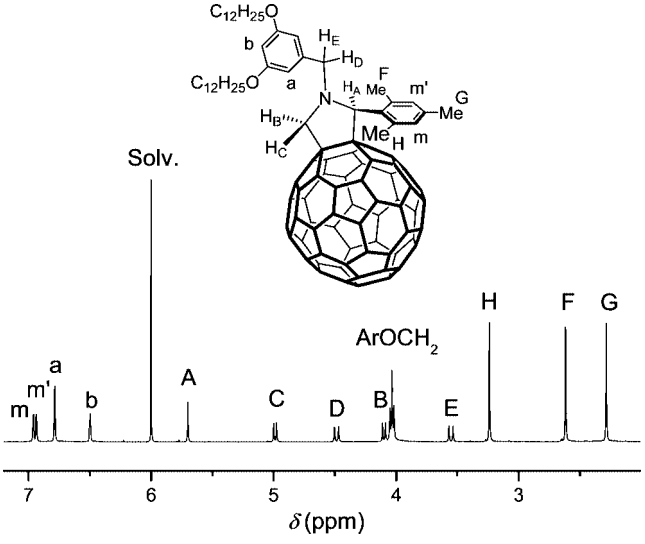


Figure 3. ^{1}H NMR spectrum (400 MHz, $CDCl_2CDCl_2$) of **5f** recorded at room temperature.

field compared to that of the two other methyl units (Me_F and Me_G). This downfield shift is clearly the result of the close proximity of the fullerene sphere. Inspection of the calculated structure of **5f** reveals that Me_H is located atop a six-membered ring of the C_{60} unit, hence falling under the influence of the ring current effect of two fullerene double bonds, and so explaining the downfield shift observed in the ^{1}H NMR spectrum.

In principle, rotation of the mesityl unit around the phenyl–pyrrolidine bond should lead to the observation of dynamic exchange between H_m and $H_{m'}$ and between Me_F and Me_H. However, the ^{1}H NMR spectra recorded in $CDCl_2CDCl_2$ over a range of temperatures (from room temperature to 120 °C) are all similar, and no coalescence could be observed, thus showing that rotation of the mesityl unit does not occur under these conditions. The steric hindrance resulting from the two *ortho*-methyl groups in **5f** appears to be sufficient to increase the rotational energy barrier to the point where the dynamic exchange observed for **5a**–**b** cannot occur anymore for **5f**.

The ^{1}H NMR spectra of compounds **5g**–**i** and **5j** recorded at room temperature are all well resolved, with sharp signals for the protons of the aromatic substituent attached to the pyrrolidine ring. As a typical example, the spectrum of compound **5g** recorded in $CDCl_2CDCl_2$ at room temperature is shown in Figure 4. In addition to the diagnostic signals arising from the *N*-(3,5-didodecylbenzyl)-pyrrolidine moiety, the spectrum is characterized by two singlets at δ = 2.39 and 2.53 ppm for the two methyl groups and three sets of aromatic signals in a typical pattern for a 1,2,5-trisubstituted phenyl ring.

In principle, two diastereoisomeric conformers (**A** and **B**) can exist for compound **5g** (Figure 4). However, the ^{1}H NMR spectra recorded at temperatures from –50 to 120 °C are all similar and reveal no dynamic exchange between two conformers. The latter observation shows that only one of the two possible conformers exists for **5g**. On the basis of 2D-NOESY experiments, it was possible to determine unambiguously that **5g** adopts a conformation in which the unsubstituted *ortho* position is located atop the fullerene sphere (conformer **A**). NOE cross-peaks have been observed for the following pairs of protons: H_A/H_F, H_F/H_m, H_m/H_p, H_p/H_G, H_G/H_o, H_A/H_B, H_B/H_C in full agreement with the proposed conformation.

Similar observations have been made for those other pyrrolidinofullerene derivatives that have an *ortho*-substituted phenyl substituent. In no case is a significant change observed for the ^{1}H NMR spectra recorded at temperatures from –50 to 120 °C, thus indicating an absence of rotation of the phenyl unit on the pyrrolidine ring. Indeed, as discussed for **5g**, 2D-NOESY experiments reveal unambiguously that compounds **5h**, **5i** and **5j** all adopt the conformation in which the unsubstituted *ortho* position is located atop the fullerene sphere. Computational studies have been performed to rationalize the experimental observations. The calculated AM1 potential energy of compound **5g** as a function of the torsion angle for rotation about the bond

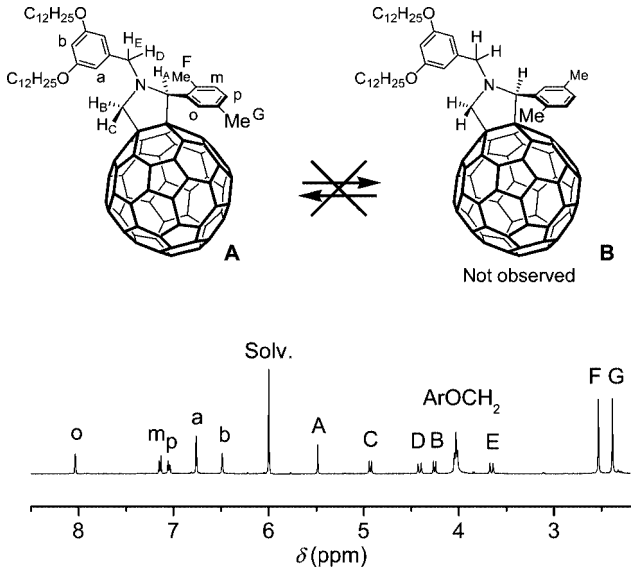


Figure 4. ^{1}H NMR spectrum (400 MHz, $CDCl_2CDCl_2$) of **5g** recorded at room temperature.

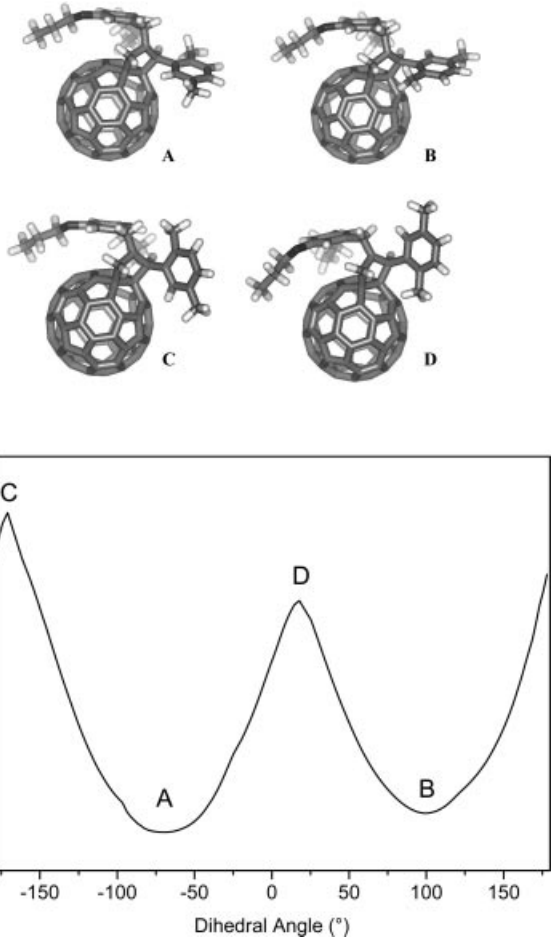


Figure 5. Bottom: calculated potential energy diagram of compound **5g** for rotation about the bond between the pyrrolidine ring and the phenyl group attached to it (the dodecyl chains have been replaced by propyl chains in the calculations). Top: theoretical structures of the four conformers corresponding to the two minima (**A** and **B**) and the two maxima (**C** and **D**).

between the pyrrolidine ring and the dimethylphenyl group is depicted in Figure 5. The calculated rotational energy barrier for rotation of the phenyl unit on the pyrrolidine ring is high (ca. 30 kcal mol^{-1}) as a result of the steric hindrance arising from the *ortho*-methyl group on the aromatic unit, thus explaining the lack of observed exchange between the two atropisomers of **5g**. However, the calculated energy difference between these two conformers is small (ca. 2 kcal mol^{-1}) and insufficient to explain the presence of only one of the two possible isomers. It is reasonable to suppose that the 1,3-dipolar cycloaddition reaction of the azomethine ylide with C_{60} is highly diastereoselective, and leads to atropisomer **A** of **5g** only. Similarly, the reaction of the other *ortho*-substituted benzaldehyde derivatives with **3** and C_{60} is diastereoselective, affording only the atropisomer in which the unsubstituted *ortho* position is located atop the fullerene unit.

Two atropisomers (**E** and **F**) are possible for compound **5d** depending on the orientation of the *meta*-methoxy substituent and variable-temperature NMR studies revealed a dynamic exchange between them (Figures 6 and 7). At room temperature, the ^{1}H NMR spectrum of **5d** shows all the expected signals, though some of them are broad. On increasing the temperature, a narrowing of these peaks is observed. This narrowing is perfectly reversible and is an unambiguous signature of the restricted rotation of the dimethoxyphenyl substituent on the pyrrolidine ring. When the ^{1}H NMR spectrum of **5d** is recorded in $CDCl_2CDCl_2$ at 100 °C (Figure 6), the dynamic exchange between the two atropisomers **E** and **F** is fast on the NMR timescale, leading to a well-resolved average spectrum for **5d** under these conditions. The spectrum is characterized by the diagnostic signals arising from the dodecyl chains, an AB quadruplet for the benzylic CH_2 unit (H_D and H_E), an AB quadruplet and a singlet for the pyrrolidine protons (H_A, H_B and H_C) as well as a singlet at δ = 3.91 ppm for the two methoxy groups and three sets of aromatic signals in a pattern typical for a 1,3,4-trisubstituted phenyl ring.

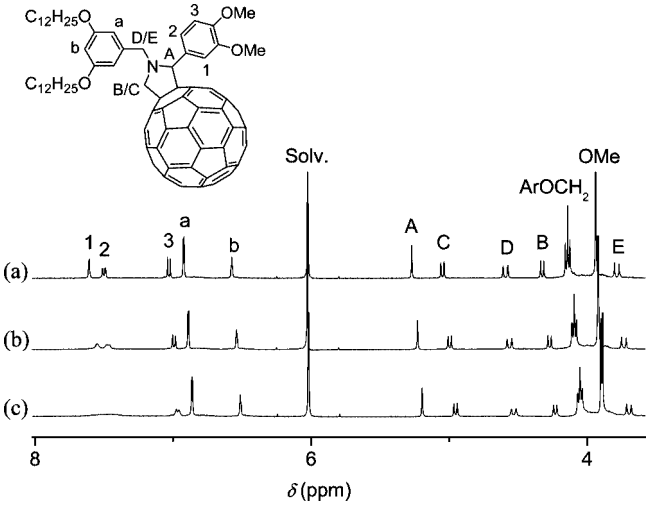


Figure 6. ^{1}H NMR spectra (400 MHz, $CDCl_2CDCl_2$) of **5d** recorded at 100 °C (a), 50 °C (b) and 30 °C (c).

By decreasing the temperature (Figure 7), a narrowing of all the peaks is also observed but the ^{1}H NMR spectrum becomes more complex. At –40 °C, the dynamic exchange between the two atropisomers is slow on the NMR timescale and the spectra of both conformers **E** and **F** are clearly observed. Interestingly, one atropisomer is present in a significantly higher proportion (ca. 65%). Detailed analysis of the spectrum recorded at –40 °C revealed **E** as the major conformer. This attribution is based on the dramatic downfield shift of H_1 in **E**, resulting from its position atop the fullerene sphere. In conformer **F**, it is $H_{2'}$ that is similarly deshielded.

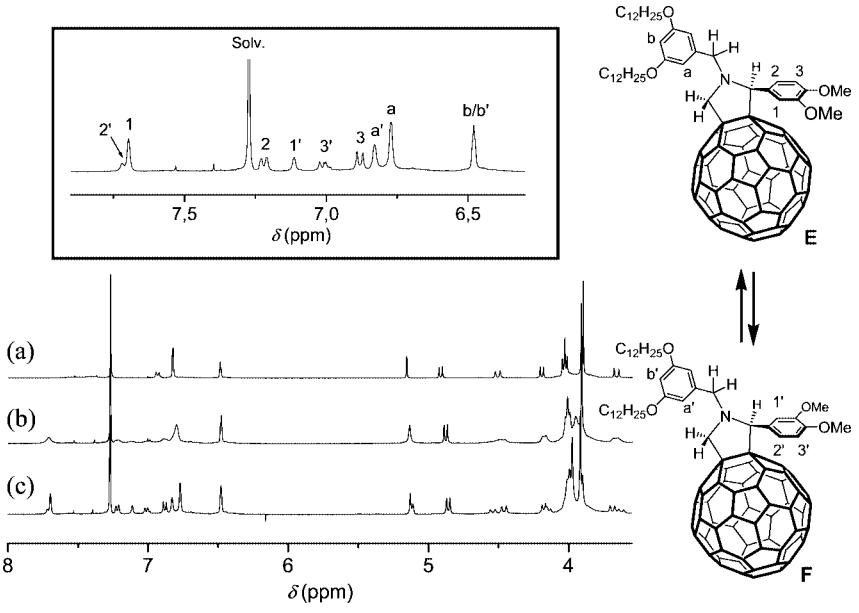


Figure 7. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of **5d** recorded at 20 °C (a), –10 °C (b) and –40 °C (c). Inset: aromatic region of the spectrum recorded at –40 °C.

Computational studies were performed in order to understand the energetics of the relative position of the dimethoxyphenyl unit and the pyrrolidinofullerene moiety in **5d** (Figure 8). Two minima were found and the rotational energy barrier between conformers **E** and **F** calculated to be ca. 15 kcal mol^{-1}. Although the calculated energy diagram depicted in Figure 8 rationalizes the observed dynamic exchange between **E** and **F**, both atropisomers have similar computed energies and there are no obvious steric reasons to explain why conformer **E** is the more abundant one at –40 °C. This prompted us to analyze the calculated dipole moment of **5d** as a function of the dihedral angle to see if the relative proportion of **E** and **F** could be controlled by electronic factors. We found a significant difference (ca. 0.7 D) between the calculated dipole moments of **E** and **F**. As one can expect, it appears that the most abundant conformer in $CDCl_3$ (**E**) is the one having the smallest μ value. To further confirm that the difference in dipole moment governs the relative **E/F** ratio, variable-temperature NMR measurements were performed in a more polar solvent, namely [D_6]acetone. The ^{1}H NMR spectrum recorded at –40 °C in this solvent clearly shows the presence of the two conformers and detailed analysis revealed that under these conditions, the atropisomer with the higher dipole moment (**F**) is present in the higher proportion (ca. 60%). The latter observation strongly suggests that the relative proportion of **E** and **F** is governed by the polarity and is thus attributable to the difference in their dipole moments.

Variable-temperature NMR studies were also carried out with compounds **5c** and **5e**. In both cases, a dynamic exchange between two atropisomers was detected and relative abundance related to their calculated dipole moments. The results are closely similar to that discussed in detail for compound **5d**.

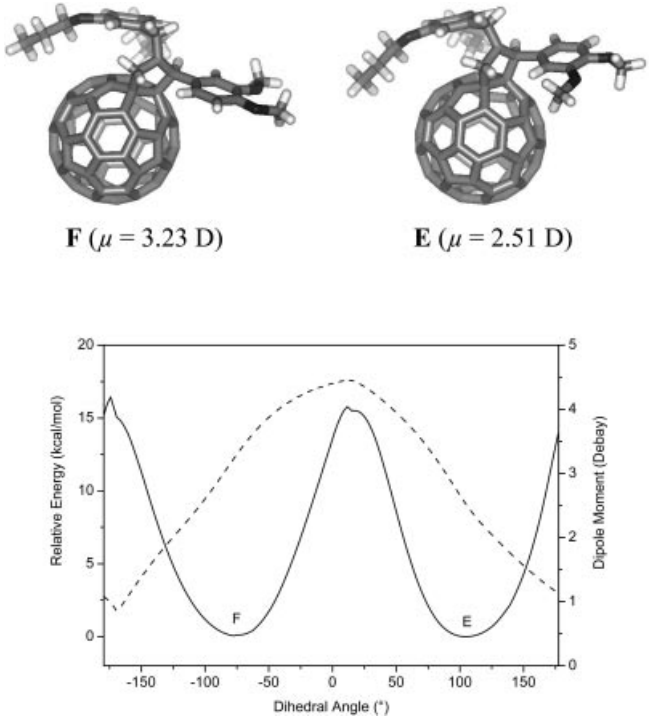


Figure 8. Bottom: calculated potential energy diagram (full line) of compound **5d** for rotation about the bond between the pyrrolidine ring and the phenyl group attached to it and calculated dipole moment (dotted line) as a function of the dihedral angle (the dodecyl chains have been replaced by propyl chains in the calculations). Top: theoretical structures of the two conformers corresponding to the two minima (**E** and **F**).

Conclusions

We have described the synthesis of a complete series of phenyl-substituted pyrrolidinofullerenes and a detailed conformational analysis based on variable-temperature ^{1}H NMR experiments and computational studies. In the case of phenyl-substituted pyrrolidinofullerene derivatives with no *ortho* substituent (**5a**–**e**), dynamic phenomena arise from restricted rotation around the phenyl–pyrrolidine bond. When both *meta* substituents are identical (**5a**–**b**), dynamic exchange is between non-equivalent protons. On the other hand, when the *meta* substituents are different, dynamic exchange between two atropisomers is observed and their relative proportion correlates with the difference in their dipole moments. In contrast, once one of the *ortho* positions of the phenyl ring is substituted (**5f**–**j**), the rotational energy barrier becomes high enough to prevent the observation of any dynamic exchange resulting from the rotation of the phenyl substituent on the pyrrolidine ring under our experimental conditions (room temperature to 120 °C). Although two diastereoisomeric conformers can exist in principle for some of the studied compounds (**5g**–**j**), only those atropisomers in which the unsubstituted *ortho* position is located atop the fullerene sphere have been observed. We conclude that the reaction of the *ortho*-substituted benzaldehyde derivatives **4g**–**j** with **3** and C_{60} must be diastereoselective, affording only one of the two possible atropisomers.

Experimental Section

General: Reagents and solvents were purchased as reagent grade and used without further purification. Compounds **1**[5a] and **4e**[8] were prepared according to literature procedures. All reactions were performed in standard glassware under Ar. Evaporation and concentration were done at water-aspirator pressure and drying in vacuo at 10^{-2} Torr. Column chromatography: silica gel 60 (230–400 mesh, 0.040–0.063 mm) from E. Merck. TLC: glass sheets coated with silica gel 60 F_{254} from E. Merck; visualization by UV light. UV/Vis spectra {λ_{max} [nm] (ε)}: Hitachi U-3000 spectrophotometer. IR spectra (ν<U=> [cm^{-1}]): ATI Mattson Genesis Series FTIR instrument. NMR spectra {δ [ppm] (J [Hz])}: Bruker AC 200 (200 MHz) or Bruker AM 400 (400 MHz); solvent peaks as reference. FAB mass spectra (*m*/*z*): ZA HF instrument; 4-nitrobenzyl alcohol as matrix. Elemental analyses were performed by the analytical service at the Institut Charles Sadron (Strasbourg, France). Molecular mechanics studies were performed with an SGI Origin 200 calculator using the Discover 3 software from MSI (www.msi.com). Partial atomic charges were evaluated by a MOPAC 6 – AM1 calculation.

Compound 2: A solution of **1** (8.0 g, 16.8 mmol), glycine ethyl ester hydrochloride (4.70 g, 33.7 mmol) and Et_3N (4.7 mL) in a 1:1 EtOH/THF mixture (240 mL) was stirred at room temp. in the presence of molecular sieves (3 Å) for 20 h. The resulting mixture was cooled to 0 °C and $NaBH_4$ (1.27 g, 33.7 mmol) was added. The reaction mixture was then slowly warmed up to room temp. and stirred for 5 h. After addition of H_2O, the mixture was extracted with CH_2Cl_2. The organic layer was then dried ($MgSO_4$), filtered and the solvents were evaporated. Column chromatography (SiO_2, CH_2Cl_2/AcOEt, 85:15) gave **2** (7.47 g, 79%) as a colorless glassy product. IR (neat): 1741 (C=O). ^{1}HNMR (200 MHz, $CDCl_3$): 0.88 (t, *J* = 6 Hz, 6 H), 1.27–1.31 (m, 39 H), 1.74 (m, 4 H), 1.87 (br. s, 1 H), 3.41 (br. s, 2 H), 3.76 (br. s, 2 H), 3.92 (t, *J* = 6 Hz, 4 H), 4.19 (q, *J* = 7 Hz, 2 H), 6.35 (t, *J* = 2 Hz, 1 H), 6.47 (d, *J* = 2 Hz, 2 H). $C_{35}H_{63}NO_4$ (561.9): C 74.82, H 11.30, N 2.49; found C 74.49, H 11.19, N 2.63.

Compound 3: An aq. 2 M KOH solution was added to a solution of **2** (4.63 g, 8.24 mmol) in a 1:1 EtOH/THF mixture (200 mL). The resulting solution was stirred at room temp. for 24 h and concentrated. After addition of water, the pH of the aq. solution was adjusted to 7 by addition of an aq. 1 M HCl solution and the mixture was extracted with CH_2Cl_2. The organic layer was then dried ($MgSO_4$), filtered and concentrated to give **3** (4.40 g, 99%) as colorless crystals. M.p. 184–185 °C. IR (CH_2Cl_2): 1701 (C=O). ^{1}HNMR (200 MHz, $CDCl_3$): 0.88 (t, *J* = 6 Hz, 6 H), 1.27–1.31 (m, 36 H), 1.65 (m, 4 H), 3.21 (br. s, 2 H), 3.80 (m, 6 H), 6.32 (t, *J* = 2 Hz, 1 H), 6.51 (d, *J* = 2 Hz, 2 H). $C_{33}H_{59}O_4N$ (533.8): C 74.25, H 11.14, N 2.62; found C 74.11, H 11.45, N 2.71.

Compound 4j: A mixture of **6** (1.03 g, 1.12 mmol) and MnO_2 (10 g) in CH_2Cl_2 (70 mL) was stirred at room temp. for 3 h. After addition of $MgSO_4$ (30 g), the mixture was filtered and the filtrate concentrated to dryness. Column chromatography (SiO_2, CH_2Cl_2/hexane, 3:7) gave **4j** (0.890 g, 87%) as a colorless liquid. ^{1}HNMR (200 MHz, $CDCl_3$): 7.38–7.69 (m, 8 H), 8.04 (d, *J* = 7 Hz, 1 H), 10.00 (s, 1 H). $C_{13}H_{10}O$ (182.2): C 85.69, H 5.53; found C 85.76, H 5.77.

Compound 5a: A solution of **4a** (129 mg, 0.555 mmol), C_{60} (400 mg, 0.555 mmol) and **3** (590 mg, 1.11 mmol) in *o*-dichlorobenzene (100 mL) was refluxed for 12 h. The mixture was cooled to room temp., filtered and the solvents were evaporated to dryness under reduced pressure. Column chromatography (SiO_2, CH_2Cl_2/Hexane, 2:8) yielded **5a** (288 mg, 37%) as a brown glassy product. UV/Vis (CH_2Cl_2): 308 (39600), 430 (4300), 702 (350). ^{1}H NMR (400 MHz, 100 °C, $C_2D_2Cl_4$): 0.97 (t, *J* = 7 Hz, 6 H), 1.30–1.50 (m, 32 H), 1.58 (m, 4 H), 1.90 (m, 4 H), 3.75 (d, *J* = 13.5 Hz, 1 H), 4.12 (t, *J* = 7 Hz, 4 H), 4.31 (d, *J* = 9.5 Hz, 1 H), 4.49 (d, *J* = 13.5 Hz, 1 H), 5.04 (d, *J* = 9.5 Hz, 1 H), 5.25 (s, 1 H), 6.56 (s, 1 H), 6.86 (s, 2 H), 7.73 (d, *J* = 7 Hz, 2 H), 7.86 (d, *J* = 7 Hz, 2 H). ^{13}C NMR (50 MHz, $CDCl_3$): 13.75, 22.27, 25.72, 28.93, 29.06, 29.22, 31.48, 67.72, 68.16, 94.08, 135.20, 135.56, 135.83, 136.35, 136.46, 139.11, 139.16, 139.46, 139.66, 141.07, 141.15, 141.36, 141.52, 141.58, 141.64, 141.71, 141.79, 142.06, 142.18, 142.51, 142.65, 143.85, 143.93, 144.08, 144.21, 144.66, 14476, 144.84, 144.99, 145.03, 145.07, 145.18, 145.46, 145.60, 145.64, 145.70, 145.80, 145.89, 146.06, 146.81, 152.38, 152.46, 153.34, 155.70, 160.09. $C_{99}H_{62}INO_2$ (1398.4): C 83.46, H 4.39, N 0.98; found C 83.33, H 4.61, N 1.10. FAB-MS: calcd. for $C_{99}H_{63}INO_2$ 1424.49; found 1424.5 [MH^+].

Compound 5b: As described for **5a**, with **4b** (98 mg, 0.555 mmol), C_{60} (400 mg, 0.555 mmol) and **3** (590 mg, 1.11 mmol) in *o*-dichlorobenzene (100 mL). Column chromatography (SiO_2, CH_2Cl_2/hexane, 2:8) yielded **5b** (258 mg, 34%) as a brown glassy product. UV/Vis (CH_2Cl_2): 255 (130800), 320 (37800), 430 (4100), 704 (420). ^{1}H NMR (300 MHz, $CDCl_3$): 0.88 (t, *J* = 7 Hz, 6 H), 1.16 (t, *J* = 7 Hz, 6 H), 1.30–1.43 (m, 32 H), 1.49 (m, 4 H), 1.83 (m, 4 H), 3.35 (q, *J* = 7 Hz, 4 H), 3.57 (d, *J* = 13.5 Hz, 1 H), 4.03 (m, 4 H), 4.12 (d, *J* = 9.5 Hz, 1 H), 4.53 (d, *J* = 13.5 Hz, 1 H), 4.88 (d, *J* = 9.5 Hz, 1 H), 5.31 (s, 1 H), 6.47 (s, 1 H), 6.72 (d, *J* = 9 Hz, 2 H), 6.99 (d, *J* = 2.5 Hz, 2 H), 7.68 (br. s, 2 H). ^{13}C NMR (50 MHz, $CDCl_3$): 12.65, 14.15, 22.70, 26.15, 29.36, 29.49, 29.71, 31.92, 44.24, 56.40, 66.42, 68.14, 68.69, 81.06, 100.16, 107.09, 11.73, 122.91, 130.51, 135.79, 135.85, 136.49, 136.62, 139.56, 139.87, 139.97, 140.06, 140.59, 141.50, 141.58, 141.77, 141.96, 142.01, 142.05, 142.11, 142.25, 142.34, 142.51, 142.59, 142.91, 143.08, 144.38, 144.69, 145.06, 145.19, 145.22, 145.26, 145.38, 145.47, 145.54, 145.61, 145.76, 145.86, 146.06, 146.11, 146.15, 146.21, 146.24, 146.59, 146.85, 147.13, 147.23, 147.94, 154.09, 154.33, 154.38, 156.91, 160.43. $C_{103}H_{72}N_2O_2{\cdot}H_2O$ (1387.7): C 89.15, H 5.37, N 2.02; found C 89.24, H 5.61, N 1.95. FAB-MS: calcd. for $C_{103}H_{72}N_2O_2$ 1369.72; found 1369.6 [M^+].

Compound 5c: As described for **5a**, with **4c** (74 mg, 0.555 mmol), C_{60} (400 mg, 0.555 mmol) and **3** (590 mg, 1.11 mmol) in *o*-dichlorobenzene (100 mL). Column chromatography (SiO_2, CH_2Cl_2/hexane, 2:8) yielded **5c** (310 mg, 42%) as a brown glassy product. ^{1}H NMR (400 MHz, 100 °C, $C_2D_2Cl_4$): 0.97 (t, *J* = 7 Hz, 6 H), 1.30–1.50 (m, 32 H), 1.58 (m, 4 H), 1.90 (m, 4 H), 2.34 (s, 3 H), 2.37 (s, 3 H), 3.73 (d, *J* = 13.5 Hz, 1 H), 4.12 (t, *J* = 7 Hz, 4 H), 4.28 (d, *J* = 9.5 Hz, 1 H), 4.55 (d, *J* = 13.5 Hz, 1 H), 5.02 (d, *J* = 9.5 Hz, 1 H), 5.24 (s, 1 H), 6.55 (s, 1 H), 6.90 (s, 2 H), 7.26 (d, *J* = 7 Hz, 1 H), 7.69 (m, 2 H). ^{13}C NMR (50 MHz, $CDCl_3$): 14.14, 19.66, 20.02, 22.71, 26.16, 26.91, 29.38, 29.50, 29.66, 29.71, 30.19, 31.94, 43.47, 56.54, 66.51, 68.20, 68.76, 81.06, 100.31, 107.34, 136.88, 140.07, 141.99, 142.02, 142.11, 142.57, 145.25, 145.26, 145.29, 145.32, 145.49, 145.51, 145.93, 146.09, 146.28, 146.29, 147.30, 153.70, 156.63, 160.51. FAB-MS: calcd. for $C_{101}H_{67}NO_2$ 1326.65; found 1326.3 [M^+].

Compound 5d: As described for **5a**, with **4d** (92 mg, 0.555 mmol), C_{60} (400 mg, 0.555 mmol) and **3** (590 mg, 1.11 mmol) in *o*-dichlorobenzene (100 mL). Column chromatography (SiO_2, CH_2Cl_2/toluene, 4:6) yielded **5d** (150 mg, 40%) as a brown glassy product. UV/Vis (CH_2Cl_2): 255 (100700), 309 (40600), 430 (4700), 704 (230). ^{1}H NMR (400 MHz, 100 °C, $C_2D_2Cl_4$): 0.97 (t, *J* = 7 Hz, 6 H), 1.31–1.52 (m, 32 H), 1.56 (m, 4 H), 1.90 (m, 4 H), 3.77 (d, *J* = 14 Hz, 1 H), 3.91 (s, 6 H), 4.12 (t, *J* = 7 Hz, 4 H), 4.31 (d, *J* = 9.5 Hz, 1 H), 4.57 (d, *J* = 14 Hz, 1 H), 5.03 (d, *J* = 9.5 Hz, 1 H), 5.25 (s, 1 H), 6.56 (t, *J* = 2 Hz, 1 H), 6.91 (d, *J* = 2 Hz, 2 H), 7.01 (d, *J* = 8 Hz, 1 H), 7.48 (dd, *J* = 8, *J* = 2, 1 H) 7.60 (d, *J* = 2 Hz, 1 H). ^{13}C NMR (50 MHz, $CDCl_3$): 14.14, 22.69, 26.12, 29.36, 29.46, 29.63, 29.70, 31.92, 55.79, 60.08, 56.41, 66.45, 68.17, 68.62, 76.81, 80.77, 100.22, 107.27, 129.36, 135.90, 136.41, 136.62, 139.80, 139.89, 140.05, 140.13, 141.55, 141.78, 141.86, 141.98, 142.08, 142.13, 142.21, 142.26, 142.54, 142.65, 142.96, 143.13, 144.35, 144.39, 144.68, 145.11, 145.25, 145.49, 145.54, 145.70, 145.92, 146.07, 146.15, 146.21, 146.28, 146.44, 146.90, 147.28, 149.04. FAB-MS: calcd. for $C_{101}H_{67}NO_4$ 1358.65; found 1358.7 [M^+].

Compound 5e: As described for **5a**, with **4e** (190 mg, 0.555 mmol), C_{60} (400 mg, 0.555 mmol) and **3** (590 mg, 1.11 mmol) in *o*-dichlorobenzene (100 mL). Column chromatography (SiO_2, CH_2Cl_2/hexane, 2:8) yielded **5e** (324 mg, 38%) as a brown glassy product. UV/Vis (CH_2Cl_2): 230 (94400), 309 (38300), 430 (4900), 705 (330). ^{1}H NMR (400 MHz, 100 °C, $C_2D_2Cl_4$): 0.97 (t, *J* = 7 Hz, 6 H), 1.30–1.50 (m, 32 H), 1.58 (m, 4 H), 1.90 (m, 4 H), 3.68–3.79 (m, 12 H), 3.89–3.95 (m, 5 H), 4.13 (t, *J* = 7 Hz, 4 H), 4.24 (t, *J* = 5 Hz, 4 H), 4.30 (d, *J* = 9.5 Hz, 1 H), 4.57 (d, *J* = 13.5 Hz, 1 H), 5.02 (d, *J* = 9.5 Hz, 1 H), 5.24 (s, 1 H), 6.56 (t, *J* = 2 Hz, 1 H), 6.90 (d, *J*

= 2 Hz, 2 H), 7.03 (d, *J* = 8 Hz, 1 H), 7.49 (dd, *J* = 8, *J* = 2, 1 H), 7.59 (d, *J* = 2 Hz, 1 H). ^{13}C NMR (50 MHz, $CDCl_3$): 14.10, 22.65, 26.10, 29.32, 29.44, 29.60, 29.66, 31.87, 56.42, 66.37, 68.11, 68.56, 68.75, 69.05, 69.44, 69.54, 70.65, 70.74, 76.75, 80.66, 100.22, 107.20, 129.69, 135.71, 135.83, 136.32, 136.41, 139.62, 139.78, 139.98, 140.06, 141.55, 141.75, 141.84, 141.97, 142.16, 142.22, 142.47, 142.58, 142.89, 143.06, 144.32, 144.62, 145.05, 145.21, 145.43, 145.66, 145.87, 146.00, 146.05, 146.16, 146.41, 146.83, 147.22, 149.05, 153.40, 153.82, 154.05, 156.42, 160.46. $C_{109}H_{81}NO_8 \cdot 2H_2O$ (1568.9): C 83.45, H 5.46, N 0.89; found C 83.18, H 5.70, N 1.12. FAB-MS: calcd. for $C_{109}H_{81}NaNO_8$ 1555.84; found 1555.6 [MNa^+].

Compound 5f: As described for **5a**, with **4f** (82 mg, 0.555 mmol), C_{60} (400 mg, 0.555 mmol) and **3** (590 mg, 1.11 mmol) in *o*-dichlorobenzene (100 mL). Column chromatography (SiO_2, CH_2Cl_2/hexane, 1:9) yielded **5f** (350 mg, 47%) as a brown glassy product. UV/Vis (CH_2Cl_2): 256 (105900), 309 (36700), 431 (3700), 702 (330). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$): 0.91 (t, *J* = 7 Hz, 6 H), 1.21–1.44 (m, 32 H), 1.48 (m, 4 H), 1.83 (m, 4 H), 2.28 (s, 3 H), 2.62 (s, 3 H), 3.24 (s, 3 H), 3.55 (d, *J* = 13.5 Hz, 1 H), 4.03 (t, *J* = 7 Hz, 4 H), 4.10 (d, *J* = 9.5 Hz, 1 H), 4.48 (d, *J* = 13.5 Hz, 1 H), 4.98 (d, *J* = 9.5 Hz, 1 H), 5.70 (s, 1 H), 6.5 (t, *J* = 2 Hz, 1 H), 6.78 (d, *J* = 2 Hz, 2 H), 6.97(s, 1 H), 6.99 (s, 1 H). ^{13}C NMR (50 MHz, $CDCl_3$): 22.71, 26.14, 29.36, 29.49, 29.65, 29.71, 31.93, 57.11, 66.50, 68.19, 68.91, 76.57, 100.19, 106.94, 127.24, 127.96, 128.00, 128.13, 129.92, 130.21, 130.51, 134.13, 134.96, 135.76, 136.24, 136.97, 139.29, 139.46, 140.00, 140.04, 140.48, 141.04, 141.58, 141.62, 141.74, 141.79, 141.92, 142.01, 142.05, 142.19, 142.22, 142.49, 142.53, 142.57, 142.61, 142.84, 143.07, 144.09, 144.25, 144.33, 144.50, 144.58, 145.08, 145.21, 14537, 145.40, 145.45, 145.67, 145.89, 145.92, 146.00, 146.04, 146.08, 146.20, 146.23, 146.48, 146.87, 147.22, 147.25. $C_{101}H_{67}NO_2 \cdot 2H_2O$ (1362.7): C 88.11, H 5.20, N 1.02; found C 88.14, H 5.38, N 0.98. FAB-MS: calcd. for $C_{101}H_{67}NO_2$ 1340.68; found 1340.1 [M^+].

Compound 5g: As described for **5a**, with **4g** (74 mg, 0.555 mmol), C_{60} (400 mg, 0.555 mmol) and **3** (590 mg, 1.11 mmol) in *o*-dichlorobenzene (100 mL). Column chromatography (SiO_2, CH_2Cl_2/hexane, 1:9) yielded **5g** (270 mg, 37%) as a brown glassy product. UV/Vis (CH_2Cl_2): 255 (147700), 305 (54400), 431 (5100), 704 (410). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$): 0.88 (t, *J* = 7 Hz, 6 H), 1.12–1.51 (m, 36 H), 1.83 (m, 4 H), 2.39 (s, 3 H), 2.53 (s, 3 H), 3.66 (d, *J* = 13.5 Hz, 1 H), 4.03 (t, *J* = 7 Hz, 4 H), 4.26 (d, *J* = 9.5 Hz, 1 H), 4.41 (d, *J* = 13.5 Hz, 1 H), 4.93 (d, *J* = 9.5 Hz, 1 H), 5.49 (s, 1 H), 6.49 (s, 1 H), 6.76 (s, 2 H), 7.05 (d, *J* = 8 Hz, 1 H), 7.14 (d, *J* = 8 Hz, 1 H), 8.03 (s, 1 H). ^{13}C NMR (50 MHz, $CDCl_3$): 14.15, 19.10, 21.46, 22.71, 26.14, 29.36, 29.47, 29.65, 29.70, 31.93, 56.32, 66.27, 68.14, 69.02, 75.95, 76.54, 100.22, 107.48, 128.80, 130.33, 130.97, 134.27, 134.66, 135.47, 135.87, 135.95, 136.49, 136.59, 139.46, 139.65, 139.78, 140.05, 140.21, 141.52, 141.62, 141.84, 141.98, 142.01, 142.09, 142.14, 142.21, 142.33, 142.53, 142.56, 142.59, 142.62, 142.94, 143.12, 144.30, 144.38, 144.62, 145.14, 145.22, 145.26, 145.30, 145.37, 145.45, 145.49, 145.56, 145.73, 145.91, 146.07, 146.10, 146.15, 146.24, 146.42, 146.63, 147.28, 153.73, 154.10, 154.16, 156.81, 160.46. $C_{101}H_{67}NO_2$ (1326.6): C 91.44, H 5.09, N 1.06; found C 91.58, H 5.43, N 1.12. FAB-MS: calcd. for $C_{101}H_{68}NO_2$ 1327.65; found 1327.1 [MH^+].

Compound 5h: As described for **5a**, with **4h** (92 mg, 0.555 mmol), C_{60} (400 mg, 0.555 mmol) and **3** (590 mg, 1.11 mmol) in *o*-dichlorobenzene (100 mL). Column chromatography (SiO_2, CH_2Cl_2/toluene, 2:3) yielded **5h** (410 mg, 54%) as a brown glassy product. UV/Vis (CH_2Cl_2): 255 (141700), 320 (51400), 430 (4900), 704 (430). ^{1}H NMR (400 MHz, $CDCl_3$): 0.90 (t, *J* = 7 Hz, 6 H), 1.24–1.55 (m, 36 H), 1.84 (m, 4 H), 3.66 (d, *J* = 13.5 Hz, 1 H), 3.72 (s, 3 H), 3.83 (s, 3 H),4.04 (t, *J* = 7 Hz, 4 H), 4.22 (d, *J* = 9.5 Hz, 1 H), 4.54 (d, *J* = 13.5 Hz, 1 H), 4.91 (d, *J* = 9.5 Hz, 1 H), 5.81 (s, 1 H), 6.49 (t, *J* = 2 Hz, 1 H), 6.85 (m, 4 H), 7.77 (d, *J* = *3* Hz, 1 H). $C_{101}H_{67}NO_4 \cdot H_2O$ (1376.7): C 88.11, H 5.05, N 1.02; found C 88.12, H 5.43, N 1.03. FAB-MS: calcd. for $C_{101}H_{68}NO_4$ 1359.65; found 1359.7 [MH^+].

Compound 5i: As described for **5a**, with **4i** (103 mg, 0.555 mmol), C_{60} (400 mg, 0.555 mmol) and **3** (590 mg, 1.11 mmol) in *o*-dichlorobenzene (100 mL). Column chromatography (SiO_2, CH_2Cl_2/hexane, 1:9) yielded **5i** (390 mg, 51%) as a brown glassy product. UV/Vis (CH_2Cl_2): 256 (128100), 309 (44500), 431 (4200), 702 (370). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$): 0.89 (t, *J* = 7 Hz, 6 H), 1.18–1.53 (m, 36 H), 1.83 (m, 4 H), 3.68 (d, *J* = 13.5 Hz, 1 H), 4.04 (m, 5 H), 4.29 (d, *J* = 9.5 Hz, 1 H), 4.38 (d, *J* = 13.5 Hz, 1 H), 4.93 (d, *J* = 9.5 Hz, 1 H), 5.86 (s, 1 H), 6.49 (broad s, 1 H), 6.79 (d, *J* = 2 Hz, 2 H), 7.22–7.34 (m, 1 H), 7.45–7.52 (m, 1 H), 7.66 (d, *J* = *8* Hz, 1 H), 8.30 (d, *J* = 8 Hz, 1 H). ^{13}C NMR (50 MHz, $CDCl_3$): 14.15, 22.71, 26.14, 29.36, 29.49, 29.71, 31.93, 56.51, 66.10, 68.19, 68.96, 76.07, 78.23, 100.30, 107.31, 125.74, 128.04, 129.85, 131.80, 133.59, 135.23, 136.16, 136.27, 136.32, 136.75, 139.70, 141.63, 141.70, 141.79, 141.94, 142.02, 142.09, 142.17, 142.21, 142.53, 142.57, 142.62, 142.99, 144.38, 144.57, 145.13, 145.32, 145.62, 145.96, 146.05, 146.08, 146.13, 146.20, 146.56, 146.71, 147.31, 153.27, 153.65, 153.97, 156.70, 160.56. $C_{99}H_{62}BrNO_2 \cdot H_2O$ (1395.5): C 85.21, H 4.62, N 1.00; found C 85.22, H 4.87, N 0.95. FAB-MS: calcd. for $C_{99}H_{63}BrNO_2$ 1378.49; found 1378.7 [MH^+].

Compound 5j: As described for **5a**, with **4j** (101 mg, 0.555 mmol), C_{60} (400 mg, 0.555 mmol) and **3** (590 mg, 1.11 mmol) in *o*-dichlorobenzene (100 mL). Column chromatography (SiO_2, CH_2Cl_2/hexane, 1:9) yielded **5j** (380 mg, 50%) as a brown glassy product. UV/Vis (CH_2Cl_2): 256 (108500), 308 (37100), 431 (3600), 704 (250). ^{1}H NMR (400 MHz, $C_2D_2Cl_4$): 0.89 (t, *J* = 7 Hz, 6 H), 1.18–1.53 (m, 36 H), 1.83 (m, 4 H), 3.53 (d, *J* = 13.5 Hz, 1 H), 4.00 (d, *J* = 9.5 Hz, 1 H), 4.05(d, *J* = 7 Hz, 4 H), 4.66 (d, *J* = 13.5 Hz, 1 H), 4.86 (d, *J* = 9.5 Hz, 1 H), 5.55 (s, 1 H), 6.49 (s, 1 H), 6.93 (s, 2 H), 7.25–7.45 (m, 7 H), 7.54 (t, *J* = 7 Hz, 1 H), 8.41 (d, *J* = 8 Hz, 1 H). ^{13}C NMR (50 MHz, $CDCl_3$): 14.15, 22.71, 26.14, 26.36, 29.49, 29.65, 29.71, 30.03, 31.93, 51.11, 66.50, 68.19, 68.91, 76.57, 77.46, 100.19, 106.94, 127.24, 127.96, 128.00, 128.13, 129.92, 134.13, 134.96, 135.76, 136.24, 136.97, 139.29, 139.46, 140.00, 140.04, 140.48, 141.04, 141.58, 141.62, 141.74, 141.79, 141.92, 142.01, 142.05, 142.19, 142.22, 142.49, 142.53, 142.57, 142.61, 142.85, 143.07, 144.09, 144.25, 144.33, 144.50, 144.58, 145.08, 145.21, 145.37, 145.40, 145.45, 145.67, 145.89, 145.92, 146.00, 146.04, 146.08, 146.20, 146.23, 146.48, 146.87, 147.22, 147.25, 153.30, 153.55, 153.79, 156.86, 160.57. $C_{105}H_{67}NO_2 \cdot H_2O$ (1392.7): C 90.55, H 5.00, N 1.01; found C 90.15, H 5.46, N 0.98. FAB-MS: calcd. for $C_{105}H_{67}NO_2$ 1374.69; found 1374.7 [M^+].

Acknowledgments

This work was supported by the CNRS, the EU (RTN Contract "FAMOUS", HPRN-CT-2002-00171) and a doctoral fellowship from the EU to T. M. F. D. We further thank L. Oswald for technical help, R. Hueber for the mass spectra and M. Schmitt for high-field NMR measurements.

[1] W. Krätschmer, L. D. Lamb, K. Fostiropoulos, D. R. Huffman, *Nature* **1990**, *347*, 354.
[2] a) F. Wudl, *Acc. Chem. Res.* **1992**, *25*, 157–161; b) F. Diederich, L. Isaacs, D. Philp, *Chem. Soc. Rev.* **1994**, *23*, 243–255; c) A. L.

Balch, M. M. Olmstead, *Chem. Rev.* **1998**, *98*, 2123–2165; d) F. Diederich, R. Kessinger, *Acc. Chem. Res.* **1999**, *32*, 537–545; e) A. Hirsch, B. Nuber, *Acc. Chem. Res.* **1999**, *32*, 795–804; f) A. de la Hoz, A. Díaz-Ortis, A. Moreno, F. Langa, *Eur. J. Org. Chem.* **2000**, 3659–3673; g) J. Nossal, R. K. Saini, L. B. Alemany, M. Meier, W. E. Billups, *Eur. J. Org. Chem.* **2001**, 4167–4171; h) A. Hirsch, O. Vostrowsky, *Eur. J. Org. Chem.* **2001**, 829–848; i) E. Nakamura, H. Isobe, *Acc. Chem. Res.* **2003**, *36*, 807–815; j) M. A. Herranz, F. Diederich, L. Echegoyen, *Eur. J. Org. Chem.* **2004**, 2299–2316.

[3] a) M. Maggini, G. Scorrano, M. Prato, *J. Am. Chem. Soc.* **1993**, *115*, 9798–9799; b) M. Prato, M. Maggini, *Acc. Chem. Res.* **1998**, *31*, 519–526.

[4] a) J.-F. Nierengarten, *New J. Chem.* **2004**, *28*, 1177–1191; b) J.-F. Nierengarten, *Sol. Energy Mater. Sol. Cells* **2004**, *83*, 187–199.

[5] a) J.-F. Eckert, J.-F. Nicoud, J.-F. Nierengarten, S.-G. Liu, L. Echegoyen, F. Barigelletti, N. Armaroli, L. Ouali, V. Krasnikov, G. Hadziioannou, *J. Am. Chem. Soc.* **2000**, *122*, 7467–7479; b) T. Gu, C. Bourgogne, J.-F. Nierengarten, *Tetrahedron Lett.* **2001**, *42*, 7249–7252; c) Y. Rio, G. Accorsi, H. Nierengarten, J.-L. Rehspringer, B. Hönerlage, G. Kopitkovas, A. Chugreev, A. Van Dorsselaer, N. Armaroli, J.-F. Nierengarten, *New J. Chem.* **2002**, *26*, 1146–1154; d) J.-F. Nierengarten, T. Gu, G. Hadziioannou, D. Tsamouras, V. Krasnikov, *Helv. Chim. Acta* **2004**, *87*, 2948–2966.

[6] a) P. De la Cruz, A. de la Hoz, L. M. Font, F. Langa, M. C. Perez-Rodriguez, *Tetrahedron Lett.* **1998**, *39*, 6053–6056; b) B. Illescas, M. A. Martínez-Grau, M. L. Torres, J. Fernández-Gadea, N. Martín, *Tetrahedron Lett.* **2002**, *43*, 4133–4136; c) M. D. L. de la Torre, G. L. Marcorin, G. Pirri, A. C. Tomé, A. M. S. Silva, J. A. S. Cavaleiro, *Tetrahedron Lett.* **2002**, *43*, 1689–1691; d) M. Suárez, Y. Verdecia, B. Illescas, R. Martínez-Alvarez, A. Alvarez, E. Ochoa, C. Seoane, N. Kayali, N. Martín, *Tetrahedron* **2003**, *59*, 9179–9186.

[7] J.-F. Nierengarten, *Top. Curr. Chem.* **2003**, *228*, 87–110.

[8] T. M. Handyside, J. C. Lockhart, M. B. McDonnell, P. V. S. Rao, *J. Chem. Soc., Dalton Trans.* **1982**, 2331–2336.

Received: May 4, 2005
Published Online: July 12, 2005

